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Title

Remarkable effect of ordered mesoporous carbon support in tantalum oxide-catalyzed selective epoxidation of cyclooctene

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Abstract
The olefin epoxidation is one of the most important reactions in chemical industry. Metal oxide supports often cause drawbacks in catalytic activity and selectivity, which has been overcome by introducing hydrophobic organic groups onto the oxide supports. The present study utilizes ordered mesoporous carbon (CMK-3 and CMK-1) as structurally defined hydrophobic catalyst support. Well-dispersed tantalum oxides supported on the ordered mesoporous carbon were prepared. Their application in catalytic epoxidation of cyclooctene demonstrates that the tantalum oxide catalysts on the ordered mesoporous carbon supports show higher performances than those of the catalysts supported on activated carbon and ordered mesoporous silica SBA-15.

Key words
olefin epoxidation; mesoporous carbon; tantalum; hydrophobicity

1. Introduction

Heterogeneous, selective oxidation catalysts are attracting considerable attentions in energy-efficient and green chemical transformation. The epoxidation of olefin is one of the most important reactions for both bulk and fine chemicals [1,2]. After pioneering works using Ti-zeolites such as TS-1 [3], mesoporous mixed oxide catalysts with larger pores (e.g., Ti substituted mesoporous silica) were developed to expand its applicability to this reaction [4-10]. Another approach has been done by immobilization of active molecular complexes (e.g., Ti, Mo, Mn, W) onto heterogeneous supports via organic anchors [11-13]. Most of the catalyst systems above mentioned utilised porous siliceous oxide or other metal oxide supports (e.g., MCM-41 and SBA-15), which caused drawbacks in catalytic activity and selectivity. Although this problem has been overcome by introducing hydrophobic organic groups onto the oxide supports [14-19], limited reports have been focused on the utilisation of carbon support [20-22], which is expected to provide hydrophobic reaction environments without the need for any organic modification. One carbon material used here was carbon nanotubes [21,22], which can provide unique catalytic performance albeit irregular in structure. Alternatively, mesoporous carbon, recently invented carbon materials with high surface area and ordered pore structures in nm size [23-26], has potential usage as catalyst supports for the olefin epoxidation. The previous report using Ni catalyst deposited on mesoporous carbon had severe deactivation problem [20]. We report here preparation of well-dispersed tantalum oxide on ordered mesopourous carbon (CMK-3 [24] and CMK-1 [23]) and their application in catalytic epoxidation of cyclooctene, which showed good conversion, selectivity and reusability. These catalytic performances are higher than those of the corresponding tantalum oxide catalysts supported on activated carbon and mesopourous silica SBA-15, indicating superior effect of the ordered mesoporous carbon materials as hydrophobic and ordered catalyst support.

2. Experimental

Ordered mesoporous carbons CMK-3 [24] and CMK-1 [23] are obtained as carbon replicas of mesoporous silica SBA-15 and MCM-48, respectively.

In order to prepare carbon supported tantalum oxide catalyst, a desired amount of 0.2 M EtOH solution of tantalum(V) ethoxide (from Aldrich) and 0.1 g of carbon material were well-mixed in 5 mL of ethanol (99.5%) at room temperature for 1 h. After removing the solvent by evaporation, the solid was heated at 900^{o}C under N_2 for 2 h, giving black powder, denoted as Ta/CMK-3 and Ta/CMK-1. The same procedure was carried out for deposition of tantalum oxide onto non-porous activated carbon (AC; from Wako) and mesoporous silica SBA-15 in order to obtain Ta/AC and Ta/SBA-15, respectively, for systematic comparison of catalytic performance.

N_2 adsorption-desorption analyses were carried out at -196^{o}C with BEL Japan BELSORP-mini II. Specific surface areas of sample were calculated according to the Brunauer–Emmett–Teller (BET) method. Pore size distributions were estimated by the Barrett–Joyner–Halenda (BJH) method. Powder XRD patterns were recorded on a Rigaku MiniFlex using Cu Kα radiation (λ=1.5418 Å) at 30 kV and 15 mV. TEM image was obtained with a JEOL JEM-2000ES at an accelerating voltage of 200 kV.

The catalytic epoxidation was carried out as follows: 2.0 mmol of cyclooctene and 25 mg of catalyst were well-mixed in 2.0 mL of acetonitrile at 65°C for 10 min. Then, 4.0 mmol of 30 wt% H_2O_2 aqueous solution was added into the mixture under vigorous stirring. After reaction, a portion of suspension was analyzed by gas chromatography (Shimadzu GC-14B) equipped with a flame ionization detector (FID) and a capillary column (HR-1). The products were identified by using authentic samples. Before the recycling test, the catalyst was recovered by centrifuge, followed by washing with a mixture of acetonitrile and water and with pure

acetonitrile, and drying at 100°C in air.

3. Results and Discussion

3.1 Preparation of tantalum oxide supported on ordered mesoporous carbon

Choice of tantalum as catalytically active metal centre has been scarcely reported, except for the systems with immobilized tantalum molecular complex on mesoporous silica [19]. The tantalum species were loaded onto several types of carbon materials by impregnating tantalum ethoxide and subsequent 900°C heating under N_2 for 2h. Mesoporous carbon CMK-3 was synthesized as carbon replica from mesoporous silica SBA-15. Other carbon support materials, mesoporous carbon CMK-1 (carbon replica from mesoporous silica MCM-48) and non-porous activated carbon (AC; from Wako), were also utilised for tantalum loading.

Dependence of the dispersion of tantalum species on its loading was first examined by XRD measurements of the tantalum oxides supported on CMK-3 (Ta/CMK-3) in 1, 5 and 20 wt% loadings (Fig. 1). The XRD patterns of 1 and 5 wt% Ta/CMK-3 showed almost no characteristic peak of the Ta_2O_5 phase, indicating high dispersion of the Ta species. In contrast, 20 wt% Ta/CMK-3 gave obvious Ta_2O_5 diffraction peaks, affording an average particle size of 13 nm calculated from the Scherrer's equation. The TEM images also gave the same tendency of the dispersion (Fig. 2). The image of 20 wt% Ta/CMK-3 (Fig.2 (c)) shows formation of large tantalum oxide crystals, while those of 1 and 5 wt% Ta/CMK-3 (Fig. 2 (a) and (b)) show no obvious crystal but only the presence of periodically aligned carbon rods of CMK-3. The absence of the large tantalum oxide particles was also confirmed in the XRD patterns and the TEM images of 1 wt% Ta on CMK-1, AC, and SBA-15 (see Fig. S1 and S2 in Supplementary data).

Further quantitative analyses were conducted by N_2 adsorption experiments (Table 1 and Fig. S3 in Supplementary data). 1 and 5 wt% Ta/CMK-3 give almost the same textual parameters as those of the parent CMK-3 itself, whereas 20 wt% Ta/CMK-3 has apparently decreased BET surface area and pore volume. These results imply that the tantalum species were well-dispersed on CMK-3 at least up to Ta loading of 5 wt%.

3.2 Epoxidation of cyclooctene catalyzed by tantalum oxide supported on ordered mesoporous carbon

The catalytic activities of the supported tantalum oxides were examined in cyclooctene epoxidation with aqueous H_2O_2 (Table 2 and Fig. 3). The tantalum oxide catalyst on CMK-3 with 1 wt% loading gave a good catalytic performance, 29% conversion of cyclooctene and 88% selectivity to cyclooctene oxide in 24 h at 65°C (Table 2, entry 1). The catalyst turnover number (TON) here is as high as 370 per Ta atom. The increased loading to 5 wt% afforded a higher conversion of 62% (entry 3). The catalyst with 20 wt% loading gave significant decrease in conversion and TON (entry 4). Considering the XRD and TEM characterization of Ta/CMK-3 catalysts above mentioned, this dependence of the catalytic activity on the Ta loading indicates that higher dispersion of tantalum species is a key factor to obtain higher activity per Ta atom.

Changing the ordered mesoporous carbon support from CMK-3 to CMK-1 afforded a further improved conversion of 57% with a slightly higher selectivity of 93% (entry 5). The difference in the activity between the two mesoporous carbon supports, CMK-3 and CMK-1, might be due to the difference in 3-dimentional mesochannel structure. In contrast, usage of non-mesoporous activated carbon (AC) support resulted in a rather lower yield of 18% (entry 7). The time profile of the reaction over the catalyst on AC (Fig. 3(a)) shows rapid decrease in conversion progress, probably due to the decomposition of H_2O_2 as a side reaction. The comparison among the

carbon supports here indicates that the ordered mesoporous structure is a remarkable factor contributing to high catalytic performance of the deposited tantalum oxide.
All of the catalysts supported on carbon, with or without the ordered mesoporous structure, gave >85% epoxide selectivity. It is notable that the tantalum oxide supported on mesoporous silica SBA-15, 1 wt% Ta/SBA-15, gave only 65% selectivity (entry 8). These results clearly indicate the superiority of using carbon support materials in order to achieve high epoxide selectivity. The higher selectivity obtained with the carbon supports can be attributed to their hydrophobicity [14-18]. The hydrophobic nature of carbon supports might facilitate adsorption of olefin molecules due to their less polarity, which leads to suppress further oxidation of more polar epoxide and decomposition of H_2O_2 [27].
The reuse experiment with 1 wt% Ta/CMK-3 and Ta/CMK-1 showed similar performances with those of the first usage in conversion and selectivity (entries 2 and 6), although slight decreases in selectivity and activity were observed. The decrease in selectivity might be attributed to a possibility that H_2O_2 causes partial oxidation of hydrophobic carbon surface to present polar functionalities.

4. Conclusion

In summary, we prepared well-dispersed tantalum oxides on ordered mesoporous carbons, which exhibit excellent selectivity, turnover number and recyclability in catalytic epoxidation of cyclooctene. The high selectivity and turnover number obtained here were found to be attributed to the utilisation of ordered mesoporous carbon as a catalyst support material. The present study suggests that the hydrophobic catalysis environment for selective olefin epoxidation, which has been mainly prepared by organic modification, can be provided by use of ordered mesoporous carbon catalyst supports. The detailed studies to understand the effect of the mesoporous structure and precise tailoring of the functionality on carbon surface are to be conducted for further improvement in catalyst design using carbon support materials [28-30].

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Appendix A. Supplementary data
Supplementary data (XRD, TEM and nitrogen adsorption adsorption/desorption data) to this article can be found online at doi:10.1016/j.catcom.xxxxxx

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Legends

Fig. 1 XRD patterns of (a) CMK-3, and (b) 1 wt% , (c) 5 wt%, (d) 20 wt% Ta/CMK-3. The asterisks(*) represent the peaks of Ta_2O_5 phase.

Fig. 2 TEM images of (a) 1 wt%, (b) 5 wt%, and (c) 20 wt% Ta/CMK-3

Fig. 3 (a) Catalytic conversions of cyclooctene and (b) selectivity to cyclooctene oxide over 1 wt% Ta catalysts on CMK-3 (■), CMK-1 (●), AC (◊) and SBA-15 (Δ).

Tables

Table. 1 Nitrogen adsorption-desorption characterizations of supported tantalum oxides.

Sample	BET surface area (m^2/g)	pore volume [a] (cm^3/g)	BJH average pore diameter (nm)
CMK-3	1,081	1.22	3.5

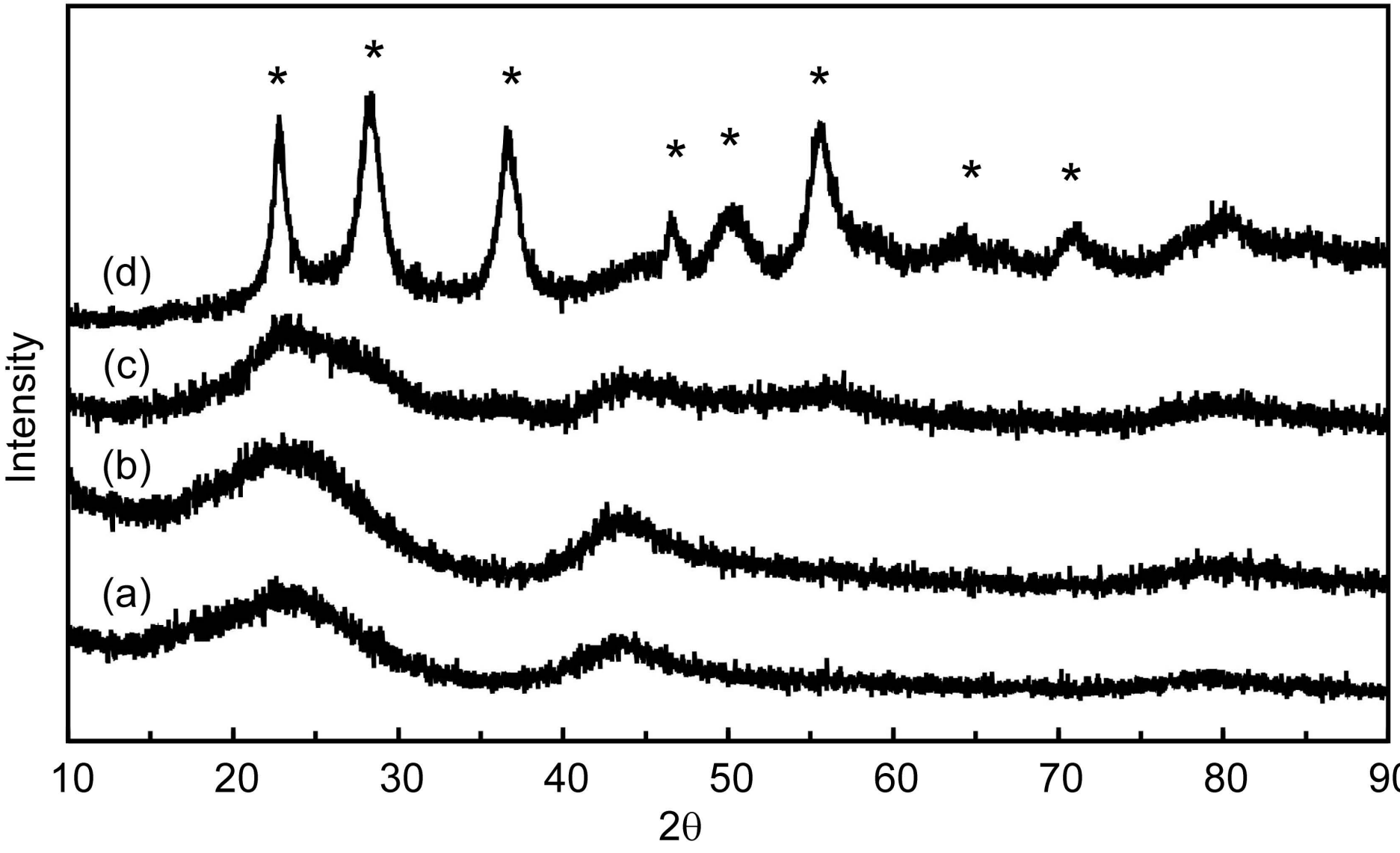
1 wt% Ta/CMK-3	1,106	1.21	3.5
5 wt% Ta/CMK-3	1,077	1.22	3.5
20 wt% Ta/CMK-3	875	0.91	3.5
1 wt% Ta/CMK-1	1,582	1.15	1.7
1 wt% Ta/AC	889	0.88	—
1 wt% Ta/SBA-15	829	1.04	6.5

[a] Total pore volume is obtained from $p/p_0 = 0.99$.

Table. 2 Epoxidation of cyclooctene catalyzed by supported tantalum oxides.[a]

Entry	Catalyst	Cyclooctene conversion (%)	Epoxide selectivity (%) [b]	Epoxide yield (%)	TON [c]
1	1 wt% Ta/CMK-3	29	88	26	370
2 [e]	1 wt% Ta/CMK-3	30	79	23	340
3	5 wt% Ta/CMK-3	62	93	57	170
4	20 wt% Ta/CMK-3	15	93	14	10
5	1 wt% Ta/CMK-1	57	93	53	760
6 [e]	1 wt% Ta/CMK-1	45	88	40	580
7	1 wt% Ta/AC	18	86	16	220
8	1 wt% Ta/SBA-15	43	65	28 [d]	400

[a] Reaction conditions: cyclooctene 2.0 mmol, H_2O_2 4.0 mmol, CH_3CN 2.0 ml, catalyst 25 mg, 65°C, 24 h. [b] Selectivity (%) = [cyclooctene oxide yield / cyclooctene conversion]*100. [c] TON = Catalyst turnover number (molar ratio of cyclooctene oxide / Ta). [d] Trace amount of side products as 2-hexene-1-ol and/or 2-hexene-1-one were detected. [e] Catalyst reuse experiment.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*
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*
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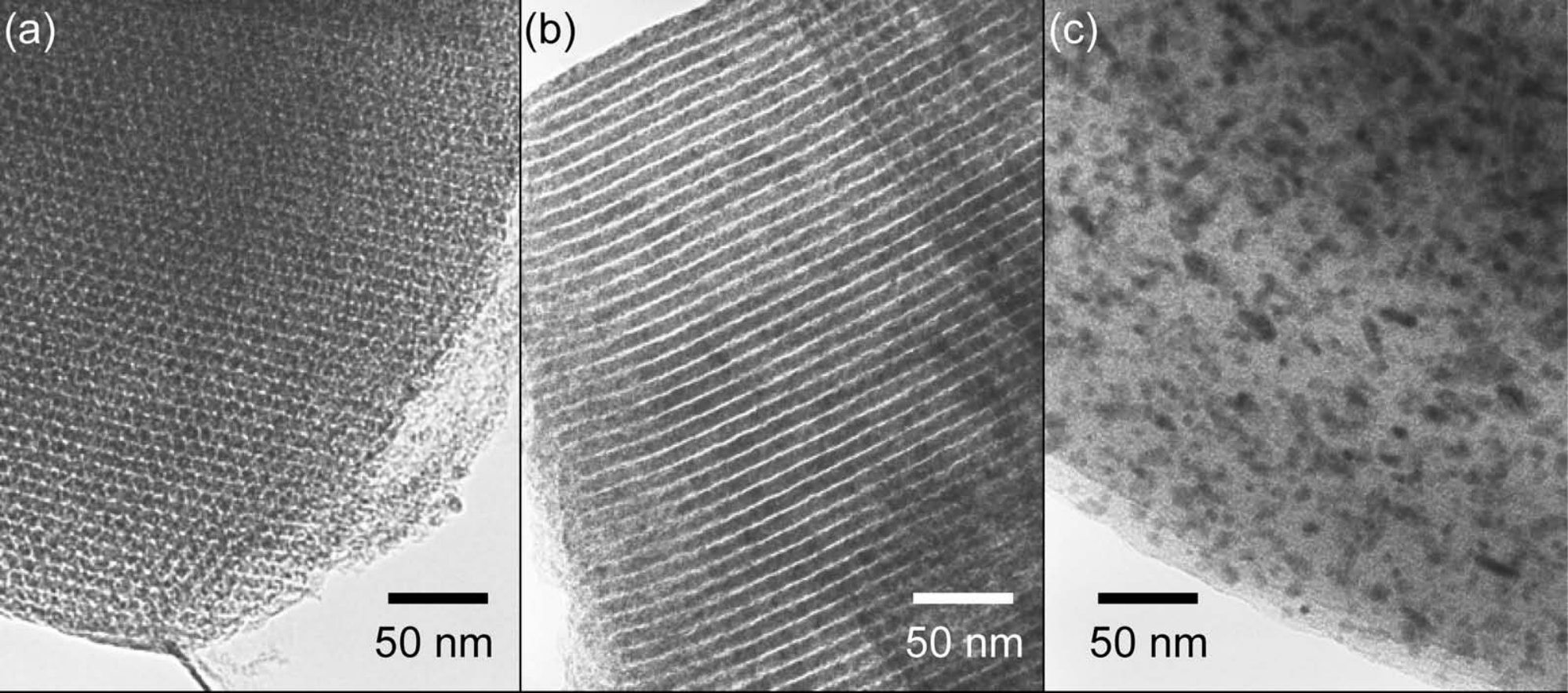
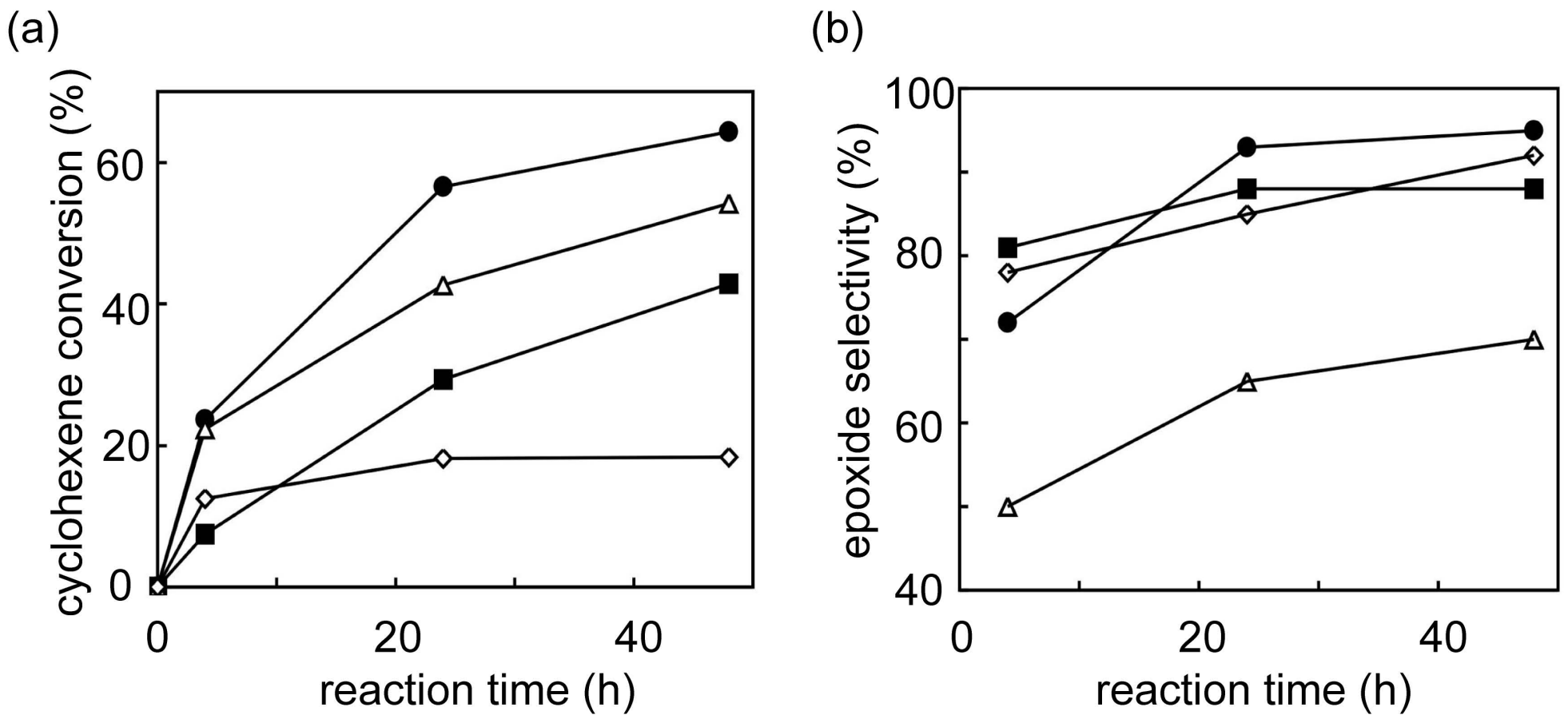
*
*
(d)
(c)
(b)
(a)
Intensity
10
20
30
40
50
60
70
80
90
2θ


(a)
50 nm
(b)
50 nm
(c)
50 nm


(a)
cyclohexene conversion (%)
0
20
40
60
0
20
40
reaction time (h)
(b)
epoxide selectivity (%)
40
60
80
100
0
20
40
reaction time (h)