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Optimization of reaction conditions for cyclohexene epoxidation with H_2O_2 over nanocrystalline mesoporous TiO_2 loaded with RuO_2

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Abstract

Cyclohexene epoxidation with H_2O_2 was performed over RuO_2/TiO_2 under various conditions. The support TiO_2 prepared by surfactant-assisted templating sol–gel method is nanocrystalline and has mesoporous structure with narrow monomodal pore size distribution. An activator of 1 mol% RuO_2 was loaded onto the synthesized TiO_2 by incipient wetness impregnation method. The resultant catalyst was characterized by XRD, N_2 adsorption–desorption and TEM analyses. Reaction conditions in the epoxidation reaction, namely reaction temperature, amount of catalyst and concentration of H_2O_2 in terms of cyclohexene/H_2O_2 ratio, were systematically optimized to obtain maximum selectivity to cyclohexene oxide.
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Keywords: Mesoporosity; RuO_2/TiO_2; Epoxidation; Cyclohexene; H_2O_2

1. Introduction

Nanocrystalline mesoporous TiO_2 generally possesses high catalytic efficiency because of its unique properties conferred by very small physical dimensions [1–3]. The large specific surface area and high volume fraction of atoms located both on the surface and at the grain boundaries result in an increased surface energy. Then, the surface of nanocrystalline TiO_2 provides an active substrate for catalysis [4]. In addition, the reactants are operated across the porous system in several applications, sufficiently uniform pore size of 2–50 nm in the mesopore region is more suitable if loading of cocatalysts/dopants is required as not to become easily blocked as in the case of microporous materials (pore size < 2 nm) [5]. Therefore, the surface of nanocrystalline TiO_2 particles with a mesoporous structural network will be more promising because catalytic activity can be further enhanced due to the enlarged surface area for facilitating better reactant accessibility to the catalysts and subsequent surface reactions [6].

Epoxidation reactions are indispensable for the chemical industry in order to produce important chemical intermediates. Unlike ordinary ethers, epoxides are quite reactive. The strained three-membered ring easily reacts with a nucleophile. By the reaction with a wide variety of nucleophiles, epoxides can be transformed into useful chemicals [7,8]. Production of epoxide by the reaction of alkenes with hydrogen peroxide (H_2O_2) is an ideal synthetic route since H_2O_2 is easy for handling and inexpensive, and possesses high content of active oxygen [9].

Alkene epoxidation with H_2O_2 generally requires a catalyst. In particular, a class of cyclohexene oxide is an important organic intermediate consumed in the production of pharmaceuticals, plant-protection agents, pesticides and stabilizers for chlorinated hydrocarbons [10]. Much effort has been dedicated to the development of new active and selective catalysts for cyclohexene epoxidation that circumvent the formation of large amounts of by-products because several side reactions can take place, such as oxidation in the allylic positions, ring-opening of the epoxides

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by hydrolysis or solvolysis, epoxide rearrangement or even total breakdown of the C=C double bonds. Cyclohexene epoxidation to yield cyclohexene oxide is also one of the most difficult cases since the first two problems, namely allylic oxidation and epoxide ring-opening, occur considerably [11].

So far, the utilization of RuO_2 in catalysis field has been considerably focused for a plenty of reactions by being loaded on various kinds of support, such as RuO_2/TiO_2 [12], RuO_2/Fe_2O_3 [13], RuO_2/WO_3 [14], $RuO_2/M_2Sb_2O_7$ (M = Ca, Sr) [15] and RuO_2/zeolite Y [16] for water splitting reaction, RuO_2/Al_2O_3 for wet air oxidation of ammonia [17] and RuO_2/CeO_2 for wet oxidation of acetic acid [18]. To our knowledge, it (in oxide form of RuO_2) has not yet been applied for any epoxidation reactions. However, only Ru in many complex forms has been extensively used for numerous epoxidation reactions, such as epoxidation of propene, octene, cyclohexene, cyclooctene, styrene, etc. [19–26]. Therefore, it is a good probability to extend the application of supported RuO_2 for the first time in catalytic cyclohexene epoxidation.

In our previous works, nanocrystalline mesoporous TiO_2 prepared by a surfactant-assisted templating sol–gel process [27] was used for cyclohexene epoxidation for the first time. The mesoporous TiO_2 showed superior catalytic performance for cyclohexene epoxidation to non-mesoporous commercial TiO_2 powders. Its catalytic performance was drastically enhanced by loading with RuO_2 at optimum content of 1 mol%, resulting in high selectivity to cyclohexene oxide [28]. In this contribution, the RuO_2-loaded nanocrystalline mesoporous TiO_2 catalyst was utilized to examine the effects of several reaction parameters in the cyclohexene epoxidation reaction in order to attain optimized conditions for maximum cyclohexene oxide selectivity.

2. Experimental

2.1. Catalyst preparation

Synthesis procedure of nanocrystalline mesoporous TiO_2 has been reported previously [27,28]. RuO_2-loaded TiO_2 catalyst was prepared by an incipient wetness method with an appropriate amount of aqueous solution of $Ru(NO)(NO_3)_3$. The impregnated TiO_2 catalyst was then dried at 80 °C and finally calcined at 500 °C for 6 h.

2.2. Catalyst characterizations

X-ray diffraction (XRD) was used to identify phases present in the samples. A Rigaku RINT-2100 rotating anode XRD system generating monochromated Cu Kα radiation with continuous scanning mode at rate of 2° min^{-1} and operating conditions of 40 kV and 40 mA was used to obtain XRD pattern. A nitrogen adsorption system (BEL Japan BELSORP-18 Plus) was employed to measure adsorption–desorption isotherms at liquid nitrogen temperature of −196 °C. The Brunauer–Emmett–Teller (BET) approach using adsorption data over the relative pressure ranging from 0.05 to 0.35 was utilized to determine specific surface area. The Barrett–Joyner–Halenda (BJH) approach was used to yield mean pore size and pore size distribution from desorption data. The sample was degassed at 200 °C for 2 h to remove physisorbed gases prior to the measurement. The sample morphology was observed by a transmission electron microscope (TEM, JEOL JEM-200CX) operated at 200 kV.

2.3. Catalytic activity measurement

The catalytic activity test was carried out without precautions against molecular oxygen in air. Within a round-bottom glass tube placed in a temperature-controlled chamber, the catalyst (10–50 mg) was added to a solution of cyclohexene (0.5 ml, 5 mmol) in *tert*-butanol (5 ml). The reaction mixture was stirred with magnetic stirrer at 1000 rpm and heated until the reaction temperature was finally maintained at a desired value (40–70 °C). The reaction was then started by the addition of an aqueous solution of 30 wt.% H_2O_2 (0.04–0.79 ml, 0.5–10 mmol) into the mixture. After 3 h of further stirring, aliquot was withdrawn from the reaction mixture, filtered and injected to a gas chromatograph (Shimadzu, GC-14B, PEG-20 M, N_2 as carrier gas) equipped with a flame ionization detector (FID) for determination of products composition. Control experiments, reacting cyclohexene in *tert*-butanol with H_2O_2 in the absence of catalyst, were also comparatively investigated. Identification of the products was performed using a gas chromatograph-mass spectrometer (Hewlett Packard, G1800A) with an electron ionization detector. The analysis revealed that the main products from the reaction are cyclohexene oxide (desired product), cyclohex-2-en-1-ol (undesired product) and cyclohex-2-en-1-one (undesired product). Selectivity is always calculated with respect to the converted cyclohexene.

3. Results and discussion

3.1. Catalyst characterizations

The crystalline phases of the synthesized catalyst were investigated using XRD analysis. XRD pattern of the RuO_2/TiO_2 catalyst is shown in Fig. 1. The main peaks at 2θ of 25.2°,

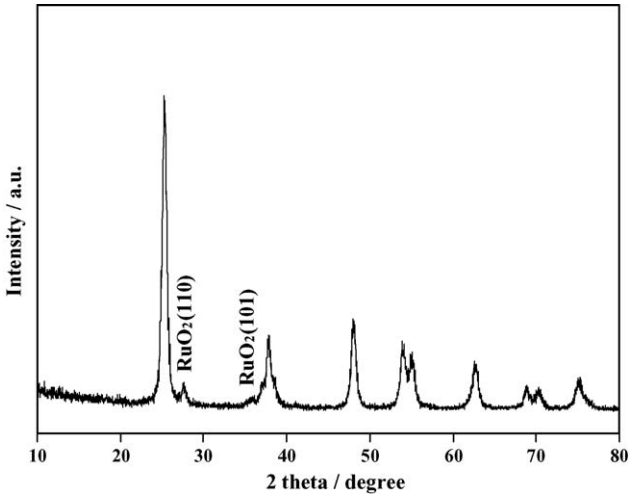

Fig. 1. XRD pattern of RuO_2/TiO_2 catalyst.

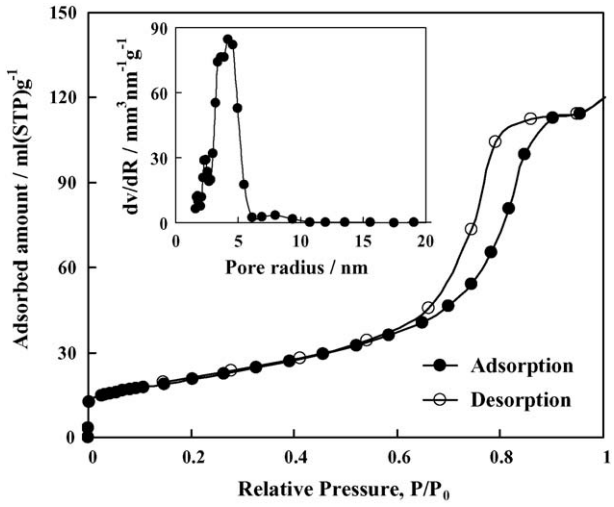

Fig. 2. N_2 adsorption–desorption isotherm and pore size distribution (inset) of RuO_2/TiO_2 catalyst.

37.9°, 47.8°, 53.8° and 55.0°, which represent the indices of (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 1 1) planes, respectively, are ascribed to structure of anatase TiO_2. The presence of small diffraction peaks at 27.6° and 35.2° is indexed to RuO_2 (1 1 0) and (1 0 1) planes, respectively.

The N_2 adsorption–desorption measurement at liquid N_2 temperature was used to study mesoporosity and textural properties of the RuO_2/TiO_2 catalyst. Fig. 2 depicts the N_2 adsorption–desorption isotherm and pore size distribution of the RuO_2/TiO_2. The isotherm revealed a typical type IV sorption behavior, representing the mesoporous structure characteristic according to the classification of IUPAC [5]. A sharp increase in adsorption volume of N_2 was observed and located in the P/P_0 range of 0.5–0.9. This sharp increase can be attributed to the capillary condensation, indicating the good homogeneity of the sample and fairly small pore size since the P/P_0 position of the inflection point is related to the pore size. As shown in the inset of Fig. 2, the pore size distribution obtained from BJH method showed very narrow and monomodal in the mesopore region (2–50 nm), indicating the good quality of the catalyst prepared by this synthetic system. From N_2 adsorption–desorption and XRD analyses, the synthesized catalyst can be reliably considered as nanocrystalline mesoporous material. The textural properties of the RuO_2/TiO_2 catalyst are also given in Table 1. The catalyst possessed BET surface area of 73 $m^2\ g^{-1}$ with mean pore diameter and total pore volume of 8.38 nm and 0.20 $cm^3\ g^{-1}$, respectively. When comparing these properties with those of unloaded TiO_2 [28], it can be apparently seen that both the BET surface area and total pore volume decreased with

Table 1
Textural properties of RuO_2/TiO_2 catalyst from N_2 adsorption–desorption measurement

Properties	Value
BET surface area ($m^2\ g^{-1}$)	73
Mean pore diameter (nm)	8.38
Total pore volume ($cm^3\ g^{-1}$)	0.20

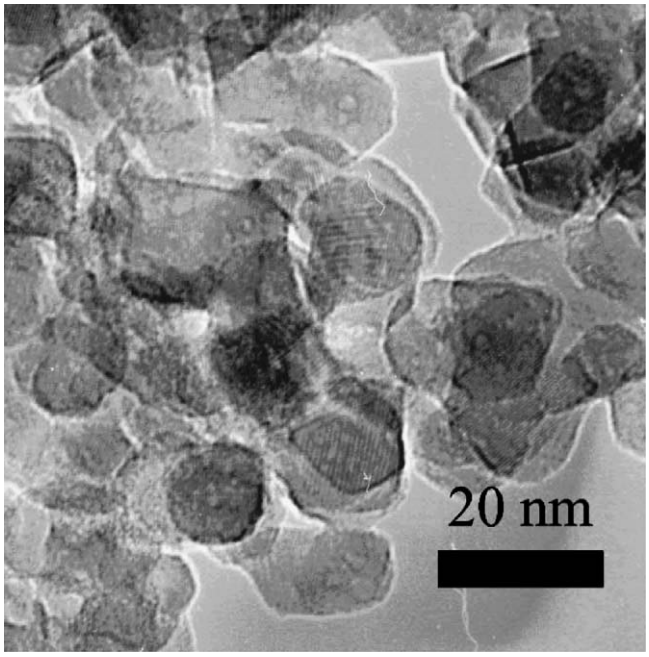

Fig. 3. TEM image of RuO_2/TiO_2 catalyst.

the RuO_2 loading, but the mean pore size conversely increased as expected. The alteration of these textural properties of the RuO_2-loaded catalyst can be plausibly owing to the effects of either the blockage of mesopore dimension with deposited RuO_2 particles or the two-step calcination process, which was required for the stabilization of the mesoporous TiO_2 catalyst regarding to the removal of surfactant template prior to the impregnation process and the activation of the RuO_2 additive at the final stage. It can be considered that the former effect might result in the decrement in all properties, whereas the latter effect might cause the decrement in the surface area and total pore volume but the increment in the mean pore size. From the experimental results, the decreased surface area and total pore volume might be attributable to the combination of both of them. However, the increase in mean pore size due to the latter effect might exceed the decrease in mean pore size due to the former effect. Thus, the increased mean pore diameter was eventually observed.

The information about morphological structure of the synthesized catalyst was obtained by TEM analysis. TEM image of the RuO_2/TiO_2 catalyst shown in Fig. 3 demonstrated the formation of nanocrystalline TiO_2 aggregates composed of three-dimensional disordered primary particles. RuO_2 was observed as deposited particles dispersed on TiO_2 particles. The observed TiO_2 particle sizes of 10–15 nm were consistent with the crystallite size estimated from XRD analysis, elucidating that each grain corresponds in average to a single crystallite. In the same manner, the particle size of the RuO_2 single crystallite was approximately 2–3 nm with some aggregations. Owing to N_2 adsorption–desorption and TEM results, the mesoporous structure of the synthesized catalyst can be attributed to the pores formed between nanocrystalline TiO_2 particles due to their aggregation, which is in the same line as the nanocrystalline mesoporous TiO_2 reported in several literatures [29–33].

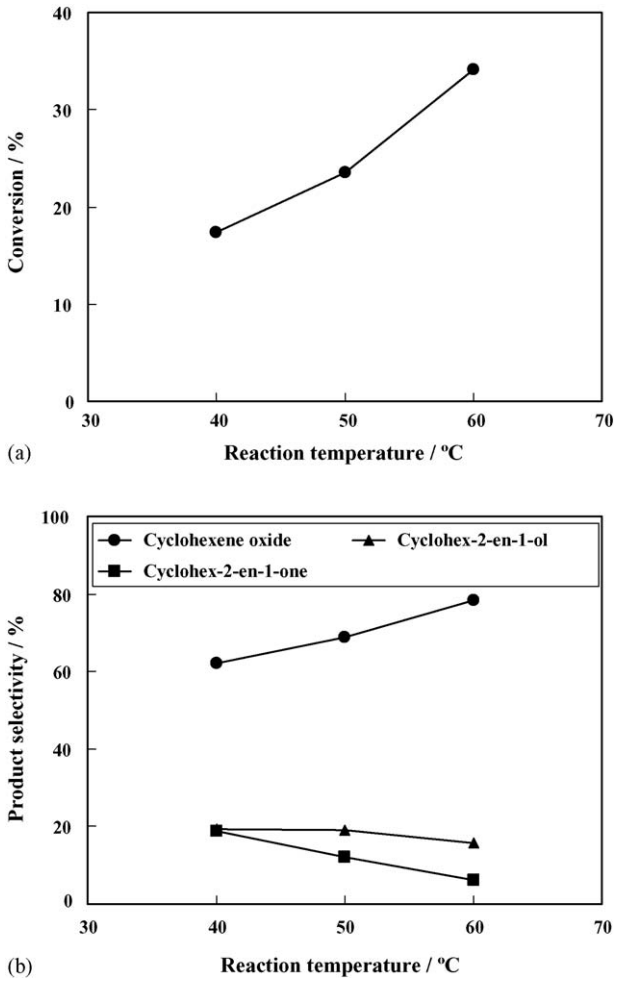

Fig. 4. Effect of reaction temperature on cyclohexene epoxidation catalyzed by RuO_2/TiO_2 catalyst: (a) cyclohexene conversion and (b) product selectivity. Reaction conditions: cyclohexene, 5 mmol; H_2O_2, 1.25 mmol; *tert*-butanol, 5 ml; catalyst, 20 mg; reaction time, 3 h.

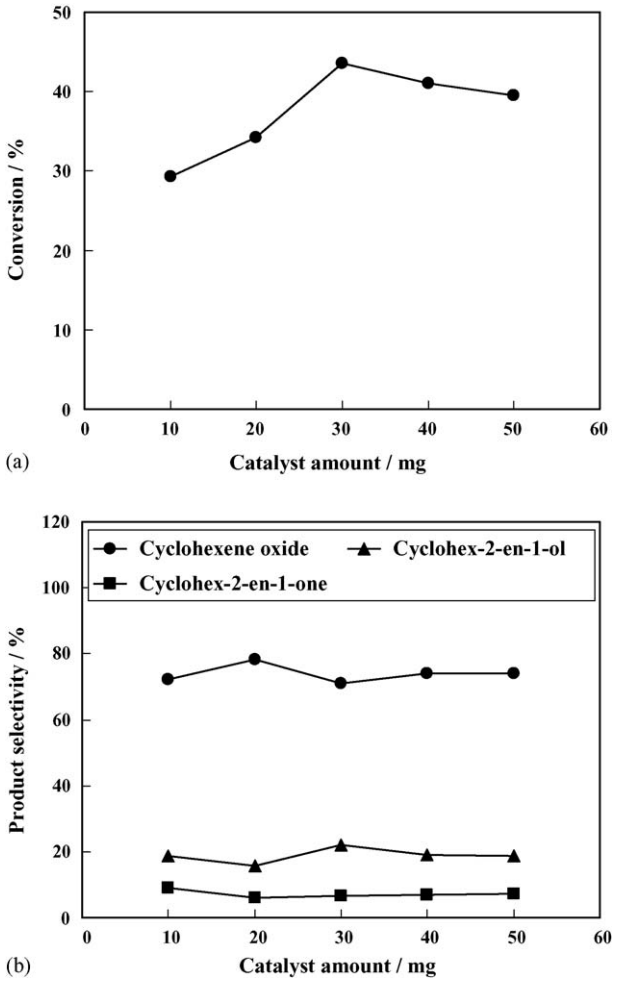

Fig. 5. Effect of catalyst amount on cyclohexene epoxidation catalyzed by RuO_2/TiO_2 catalyst: (a) cyclohexene conversion and (b) product selectivity. Reaction conditions: cyclohexene, 5 mmol; H_2O_2, 1.25 mmol; *tert*-butanol, 5 ml; reaction temperature, 60 °C; reaction time, 3 h.

3.2. Catalytic activity

From our previous work, the nanocrystalline mesoporous TiO_2 synthesized by this synthetic method exhibited high potential to be used as cyclohexene epoxidation catalyst, compared with non-mesoporous commercial TiO_2 powders, i.e. Ishihara ST-01 and Degussa P-25. In addition, the loading of 1 mol% (optimum content) of RuO_2 onto the mesoporous TiO_2 significantly enhanced the selectivity to cyclohexene oxide (desired product) [28] when compared to the loading of MO_x (M = Fe, Co, Ni, V, Mo and W). Since high selectivity to cyclohexene oxide is focused as a target for developing catalyst, the RuO_2/TiO_2 has been taken to improve cyclohexene oxide production by further optimization of reaction conditions.

The effect of reaction temperature was initially studied in the range of 40–60 °C. Over 70 °C, decomposition or vaporization of hydrogen peroxide proceeds suddenly. The results of the effect of the reaction temperature are shown in Fig. 4. It is obviously seen that both conversion and selectivity to cyclohexene oxide drastically decreased with decreasing the reaction temperature from 60 to 40 °C. On the other hand, the selectivities to the other two undesired products (cyclohex-2-en-1-ol and cyclohex-2-en-1-one) increased. This can be inferred that the reaction temperature of 60 °C is an optimum point to yield the highest cyclohexene oxide selectivity under the controllable reaction temperature interval.

The amount of catalyst was further optimized by maintaining the reaction temperature at 60 °C. The catalyst amount was increased up to 50 mg under the identical reaction conditions. The effect of catalyst amount is shown in Fig. 5. The cyclohexene conversion increased with increasing the catalyst amount until reaching the peak at 30 mg and then gradually declined. However, by considering the selectivity to cyclohexene oxide, the catalyst amount of 20 mg provided the highest cyclohexene oxide selectivity of approximately 80%, with minimum selectivities to cyclohex-2-en-1-ol and cyclohex-2-en-1-one. Similar observation has also been reported in case of α-TiRuAs/dry *tert*-butyl hydroperoxide system [34], in which the optimum catalyst amount that yielded maximum cyclohexene oxide selectivity and minimum cyclohex-2-en-1-ol and cyclohex-2-en-1-one selectivities was reported. When the applied catalyst content was beyond the critical amount, the aggregation among particles during

suspension might be more pronounced, resulting in loss of reactant accessibility into mesopores and subsequent lower catalytic activity. Additionally, it was mentioned that the complete absorption of water produced during the reaction can assist avoid the ring-opening of the epoxide from hydrolysis [35]. Therefore, the investigated amounts of catalyst are adequate to preserve the high catalytic performance without products from ring-opening. From these results, the optimum conditions for the reaction temperature and catalyst amount are 60 °C and 20 mg, respectively.

The concentration of H_2O_2 was also another important parameter affecting the cyclohexene oxide selectivity to be further optimized. By fixing the substrate (cyclohexene) amount constant, the effect of H_2O_2 amount was studied over a wide range of cyclohexene to H_2O_2 molar ratio from 0.5 to 10 with the RuO_2/TiO_2 catalyst (note that the previously described results were based on the ratio of 4). In order to compare the catalytic performance, the experiments without the RuO_2/TiO_2 catalyst (control experiments) were also performed at various cyclohexene/H_2O_2 ratios. In control experiments, the results from product determination reveal that the autooxidation of cyclohexene to form cyclohexene oxide and cyclohex-2-en-1-ol but with relatively low conversion was observed. This is plausibly due to the strong oxidizing power of H_2O_2, where it reacts with *tert*-butanol to initially form the in situ generated *tert*-butyl hydroperoxide, which functions as a major source of the initiator and is then thermally decomposed to generate active free radicals for autooxidation reaction with cyclohexene in the presence of dissolved molecular O_2 acting as propagating species to finally produce those oxygen-containing products [28]. Fig. 6 represents the cyclohexene conversion and product selectivities at various cyclohexene/H_2O_2 ratios both in the case of the absence and presence of the RuO_2/TiO_2 catalyst. As obviously seen in the case of the presence of the catalyst, the cyclohexene conversion was almost independent of the cyclohexene/H_2O_2 ratio in all cases at approximately 30–35% over the entire range. However, it is interestingly found that the cyclohexene oxide selectivity dramatically increased until leveling off beyond the ratio of 4 at maximum cyclohexene oxide selectivity of approximately 80% and vice versa for the cyclohex-2-en-1-ol selectivity, which noticeably declined until becoming almost unchanged at an identical value. In the meantime, the cyclohex-2-en-1-one selectivity was comparatively low only around 5–10% and its change was

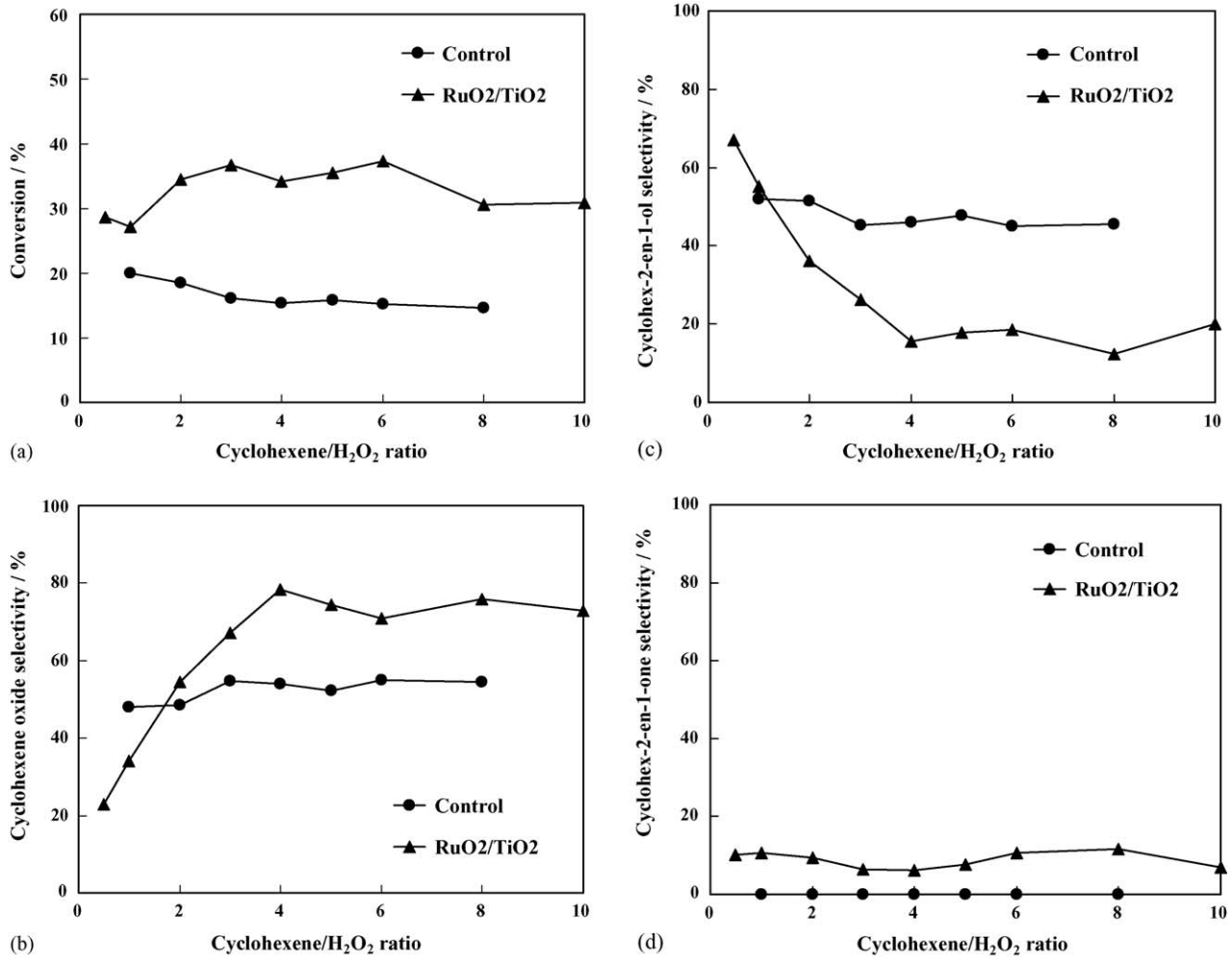

Fig. 6. Effect of cyclohexene/H_2O_2 ratio on cyclohexene epoxidation catalyzed by RuO_2/TiO_2 catalyst compared with control experiments: (a) cyclohexene conversion, (b) cyclohexene oxide selectivity, (c) cyclohex-2-en-1-ol selectivity and (d) cyclohex-2-en-1-one selectivity. Reaction conditions: cyclohexene, 5 mmol; *tert*-butanol, 5 ml; catalyst, 20 mg; reaction temperature, 60 °C; reaction time, 3 h.

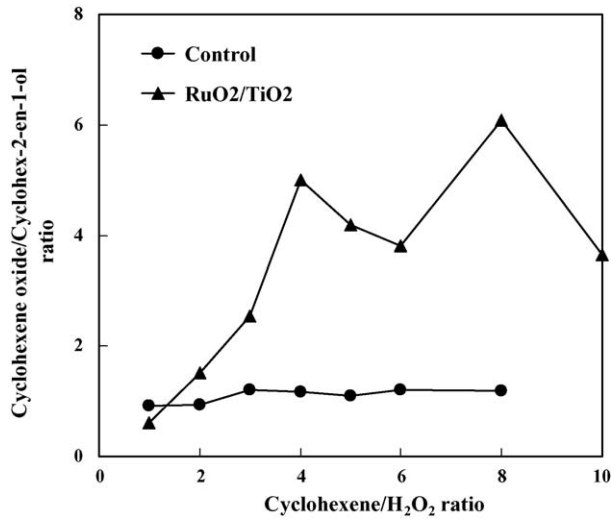

Fig. 7. Effect of cyclohexene/H_2O_2 ratio on product (cyclohexene oxide/cyclohex-2-en-1-ol) ratio from cyclohexene epoxidation catalyzed by RuO_2/TiO_2 catalyst compared with control experiments. Reaction conditions: cyclohexene, 5 mmol; *tert*-butanol, 5 ml; catalyst, 20 mg; reaction temperature, 60 °C; reaction time, 3 h.

much less than that of the other products. In contrast to the case of the presence of the catalyst, the cyclohexene conversion was relatively low around 15–20% in the case of the absence of the catalyst, whereas both the cyclohexene oxide and cyclohex-2-en-1-ol selectivities were almost at the similar level both at roughly 50% over the entire range of the cyclohexene/H_2O_2 ratio. Besides, no cyclohex-2-en-1-one was observed at any conditions. Therefore, the cyclohexene/H_2O_2 ratio of 4 is sufficient to attain satisfactorily high cyclohexene oxide selectivity.

Since the main products from the reaction are cyclohexene oxide (desired product) and cyclohex-2-en-1-ol (undesired product), it is worth demonstrating the product ratio to evaluate the catalytic performance of the catalyst in comparison with the case of control experiments at various cyclohexene/H_2O_2 ratios. Fig. 7 shows the comparison of the cyclohexene oxide/cyclohex-2-en-1-ol ratio over the entire range of the cyclohexene/H_2O_2 ratio. It is evident that especially beyond the cyclohexene/H_2O_2 ratio of 4, the product ratio in the case of the RuO_2/TiO_2 catalyst was much higher than that in the case of the control experiments without the catalyst, of which the product ratio was approximately 1 over the entire range of the cyclohexene/H_2O_2 ratio. As can be seen from Figs. 6 and 7 in the case of the absence of the catalyst over such the entire range that both almost constant cyclohexene conversion and product (cyclohexene oxide and cyclohex-2-en-1-ol) selectivities with nearly the same molar product formation were observed, it can be supposed that the amount of dissolved molecular O_2, which was likely to be consistent in all experiments, was the most decisive factor determining the autooxidation activity, although different contents of the in situ generated *tert*-butyl hydroperoxide were formed. However, in the case of the presence of the catalyst, it certainly plays a crucial role in overall catalytic performance due to the surface epoxidation upon oxygen transfer reaction. Since the particular amount of catalyst (20 mg, 0.25 mmol) was used in the reaction conditions of excess *tert*-butanol, constant cyclohexene amount (5 mmol) and different H_2O_2 amounts (decreasing from 10 to 0.5 mmol in order to obtain different cyclohexene/H_2O_2 ratios increasingly ranging from 0.5 to 10), the active catalyst surface available for *tert*-butyl peroxotitanium complex formation prior to oxygen transfer reaction was then limited. At the cyclohexene/H_2O_2 ratios lower than optimum value of 4, large amount of H_2O_2 might be left in the solution phase, being able to react with cyclohexene via chain free radical reactions upon autooxidation pathway. In conjunction with the surface epoxidation reaction, this might eventually result in high cyclohex-2-en-1-ol selectivity and low cyclohexene oxide selectivity. On the contrary, at the cyclohexene/H_2O_2 ratios more than optimum value of 4, the surface oxygen transfer reaction to form cyclohexene oxide as the main product might predominantly occur, while the difference due to autooxidation might be reasonably negligible because most of H_2O_2 used probably underwent *tert*-butyl peroxotitanium complex formation for surface cyclohexene epoxidation. Consequently, the high cyclohexene oxide selectivity was attained with low undesired product selectivities, while the total amount of convertible cyclohexene through the combination of surface epoxidation and autooxidation at cyclohexene/H_2O_2 ratios more than value of 4 might be insignificantly different, causing slight change in its conversion.

The recyclability test of the catalyst for cyclohexene epoxidation with H_2O_2 in *tert*-butanol was also tested for three cycles at the obtained optimum reaction conditions. From the experimental results, it can be found that the cyclohexene conversion only slightly decreased, however the selectivity to cyclohexene oxide significantly decreased to 33 and 19% for the second and third cycles, respectively. Since the recyclability of the catalyst is very indispensable for real application, potential approaches to efficiently recover the spent catalyst should have to be essentially investigated in future work.

Finally, it can be concluded that at the optimum reaction conditions (reaction temperature, 60 °C; catalyst, 20 mg; cyclohexene/H_2O_2 ratio, 4) under the investigated system, the RuO_2-loaded nanocrystalline mesoporous TiO_2 was verified to be a promising catalyst with high catalytic performance for cyclohexene epoxidation with H_2O_2. However, the recyclability of the catalyst must be further evaluated.

4. Conclusions

Nanocrystalline mesoporous TiO_2 catalyst with narrow monomodal pore size distribution was synthesized, loaded with 1 mol% RuO_2 by incipient wetness impregnation process, and utilized as an effective catalyst for cyclohexene epoxidation with H_2O_2. Several reaction parameters in the cyclohexene epoxidation reaction, namely reaction temperature, amount of catalyst and concentration of H_2O_2 in terms of cyclohexene/H_2O_2 ratio, were optimized to acquire maximum selectivity to cyclohexene oxide. Under optimization of these parameters, maximum cyclohexene oxide selectivity up to 80% was achieved when cyclohexene/H_2O_2 ratio, catalyst amount and reaction temperature were 4, 20 mg and 60 °C, respectively.

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