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Effective Heterogeneous MoO_x-modified CeO_2 Catalyst for Michael Addition of Dimethyl Malonate to 2-Cyclohexen-1-one

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Abstract: Molybdenum oxide-modified cerium oxide (MoO_x-CeO_2) with 1 wt% Mo acted as an effective and reusable heterogeneous catalyst for Michael addition of dimethyl malonate to 2-cyclohexen-1-one, providing high yield of the target product (99%). The catalyst showed higher activity with high selectivity (>99%) than simple metal oxides and the other combination of metal oxides and CeO_2. Based on the catalyst characterization and experimental studies, MoO_x species in the MoO_x-CeO_2 catalyst are isolated Mo^{6+}, and the interface between the isolated MoO_x and CeO_2 is the active site. The activity based on the active site was about 74-fold and 1800-fold higher than that of CeO_2 surface and the typical strong organic base of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), respectively.

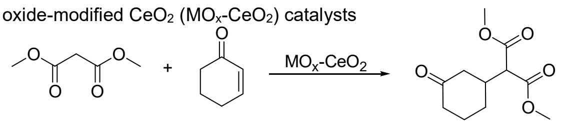
Nucleophilic addition reactions such as aldol reaction, Michael reaction, Mannich reaction and so on are of great importance in organic synthesis because they can enable the formation of a C-C or C-X (O, N, S, etc…) bond in organic compounds. Conventionally, Lewis (or Brønsted) acid or Lewis base catalysts are used for the reactions, which however suffers from the formation of salts and separation of the catalysts. To overcome the problems, various effective homogeneous[1] and heterogeneous catalysts[2] have been developed, and heterogeneous catalysts are preferable to homogenous ones in terms of the catalyst reusability and separation from reaction mixtures. Organic bases and acids immobilized on solid materials are well-known effective heterogeneous catalysts for nucleophilic addition reactions,[3] which is due to the acid-base bifunctional property. However, the stability and leaching of the organic modifiers under the reaction conditions are problematic. Strong solid base catalysts such as MgO, KF/Al_2O_3 and Mg-Al-O-*t*-Bu hydrotalcite are also reported to be effective for the reactions,[4] however, these catalysts are easily deactivated by H_2O, CO_2 and polymerized products, and the handling and reuse of the catalysts are generally difficult. On the other hand, metal hydroxides [5] such as hydrotalcite-like materials and serpentine, and metal phosphates[6] such as amorphous aluminophosphate and cerium phosphate are also reported to be effective acid-base bifunctional heterogeneous catalysts for aldol condensation and acetalization reactions. Modification of main metal oxides with other metal oxides is a typical method for controlling the acid-base and/or redox properties of metal oxides. Binary metal oxides including mixed metal oxides such as SiO_2–MgO, $Zn_xZr_yO_z$, TiO_2-ZrO_2, $Ce_xZr_{1-x}O_2$ and so on were reported to work as a strong base or acid-base bifunctional heterogeneous catalyst for nucleophilic addition reactions.[7] The reports on the effective inorganic solid catalyst systems are limited, and there is room for development of only inorganic solid catalysts with suitable acid-base property.

Cerium oxide (CeO_2) has unique acid-base and redox properties and can exhibit superior catalysis for various organic reactions at comparatively low temperature (<473 K).[8] CeO_2 shows higher activity in nucleophilic reactions with alcohols and amines as nucleophiles due to the high activation ability of the polarized functional groups.[9] CeO_2 also has some activity for the nucleophilic addition reactions with activated methylene compounds (C-C bond formation reactions),[10] and the acid-base property is proposed to play an important role in the reaction. However, the activity is generally much lower than the strong solid base catalysts such as MgO, CaO and hydrotalcite.[10a,c] We envisioned that the modification of CeO_2 with some metal oxides could improve the catalytic activity for the nucleophilic addition reactions such as aldol and Michael reactions.

Herein, we found that MoO_x-modified CeO_2 (MoO_x-CeO_2) with 1 wt% Mo was an effective heterogeneous catalyst for the Michael addition of dimethyl malonate to 2-cyclohexen-1-one, and that the activity is 74-fold and 1800-fold higher than that of CeO_2 surface and DBU(1,8-diazabicyclo[5.4.0]undec-7-ene), a typical strong organic base, respectively.

At first, the catalytic performance of simple metal oxides was tested. Michael addition of dimethyl malonate to 2-cyclohexen-1-one was conducted as a model reaction by using various simple metal oxides without pre-heating treatment. (Table S1). CeO_2, La_2O_3 and Y_2O_3 showed activity (conversion: 9, 3 and 1%, respectively) with high selectivity to the target product (>99%), and the other metal oxides (La_2O_3, Y_2O_3, ZrO_2, TiO_2, γ-Al_2O_3, SiO_2, MgO, ZnO, MoO_2, MoO_3, Mn_2O_3, Fe_2O_3, MnO, NiO and Cu_2O) have no activity in the reaction. Among the active metal oxides, CeO_2 showed higher conversion than the other metal oxides. Next, the conversion of CeO_2 and La_2O_3 under air and Ar was compared. In the case of CeO_2, the conversion under Ar (20%, selectivity: >99%) was clearly higher than that under air (9%, selectivity: >99%), while those under air and Ar were similar in the case of La_2O_3 (3%, selectivity: >99%). Therefore, we selected CeO_2 and

Table 1. Michael addition of dimethyl malonate to 2-cyclohexen-1-one with metal oxide-modified CeO_2 (MO_x-CeO_2) catalysts



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Entry	M in MO_x-CeO_2	Conversion[a] /%	Selectivity[a] /%	
			1	Others
1	Mo	53	>99	<1
2	Re	39	>99	<1
3	W	35	>99	<1
4	V	31	>99	<1
5	Mn	22	99	1
6	Nb	22	>99	<1
7	Fe	4	>99	<1
8	Mg	2	>99	<1
9	Na	2	>99	<1
10	none (CeO_2)	20	>99	<1
11	Mo(acac)$_2$	<1	-	-

Reaction conditions: 2-cyclohexen-1-one 1.0 mmol, dimethyl malonate 1.1 mmol, MO_x-CeO_2(M=1 wt%) 30 mg, toluene 1.5 mL, 303 K, 4 h, Ar. [a]These values are calculated on 2-cyclohexen-1-one basis.

Ar as the main metal oxide and reaction atmosphere, respectively in the following study.

Modification of CeO_2 catalyst with various metal oxides (MO_x) was studied (Table 1). The selectivity to the target product is high (≥99%) with all catalysts. Mo, Re, W and V provided higher conversion than CeO_2 (entries 1-4 and 10), which suggests that these metal oxides are effective additives for CeO_2 catalyst. Mn and Nb (entries 5 and 6) showed similar conversion than CeO_2, indicating that these metal oxides have no effect on the catalysis of CeO_2. Fe, Mg and Na (entries 7-9) provided negative effect on the reaction, and lower conversion (<5%) was obtained. To check the activity of a homogenous Mo complex, Mo(acac)$_2$ was applied to the reaction, showing no conversion. Among these metal oxides, MoO_x provided the highest conversion with high selectivity, and hence, MoO_x was the most effective modifier for CeO_2.

The combination of MoO_x with other metal oxides was tested in the same reaction with various MoO_x-modified metal oxide catalysts (Table 2). Modification of MgO and La_2O_3 with MoO_x showed activity (entries 2 and 3), however, the conversion (<11%) is much lower than that over CeO_2 (53%). Modification of the other metal oxides showed almost no conversion. Considering that only MoO_3 and MoO_2 have no activity in the reaction under air and Ar (Table S1), the combination of CeO_2 and MoO_x is essential for obtaining the high activity, and the interface of CeO_2 and MoO_x will be the active site.

Table 2. Michael addition of dimethyl malonate to 2-cyclohexen-1-one with MoO_x-Metal oxide catalysts

Entry	Metal oxide in MoO_x-Metal oxide	Conversion[a] /%	Selectivity[b] /%	
			1	Others
1	CeO_2	53	>99	<1
2	MgO	11	>99	<1
3	La_2O_3	3	>99	<1
4	γ-Al_2O_3	<1	-	-
5	α-Al_2O_3	<1	-	-
6	ZrO_2	<1	-	-
7	TiO_2	<1	-	-
8	SiO_2-Al_2O_3	<1	-	-
9	SiO_2	<1	-	-
10	La_2O_3	<1	-	-

Reaction conditions: 2-cyclohexen-1-one 1.0 mmol, dimethyl malonate 1.1 mmol, MoO_x-Metal oxide (Mo=1 wt%) 30 mg, toluene 1.5 mL, 303 K, 4 h, Ar. [a]These values are on 2-cyclohexen-1-one basis.

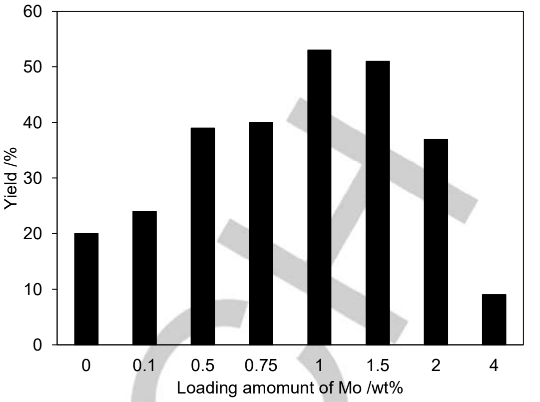

Figure 1. Effect of Mo loading amount in MoO_x-CeO_2 catalysts in Michael addition of dimethyl malonate to 2-cyclohexen-1-one

Reaction conditions: 2-cyclohexen-1-one 1.0 mmol, dimethyl malonate 1.1 mmol, MoO_x-CeO_2 30 mg, toluene 1.5 mL, 303 K, 4 h, Ar. Yield is calculated on 2-cyclohexen-1-one basis.

The effect of Mo loading amount in MoO_x-CeO_2 was investigated (Figure 1). The conversion increased with increasing the Mo loading amount up to 1 wt%, in contrast, it decreased with higher Mo loading amount than 1 wt%. Therefore, MoO_x-CeO_2 with 1 wt% Mo was the most effective catalyst for the reaction.

MoO_x-CeO_2 catalysts with different Mo loading amounts were characterized by XRD, TEM, XPS and Raman (Figure 2). XRD patterns show only the signals due to CeO_2, and the signals due to MoO_x species were not detected (Figure 2(A)). These results indicate that MoO_x species are highly dispersed or amorphous over CeO_2. Next, TEM image of MoO_x-CeO_2 with 1 wt% Mo was measured (Figure 2(B)), showing only CeO_2 particles and no

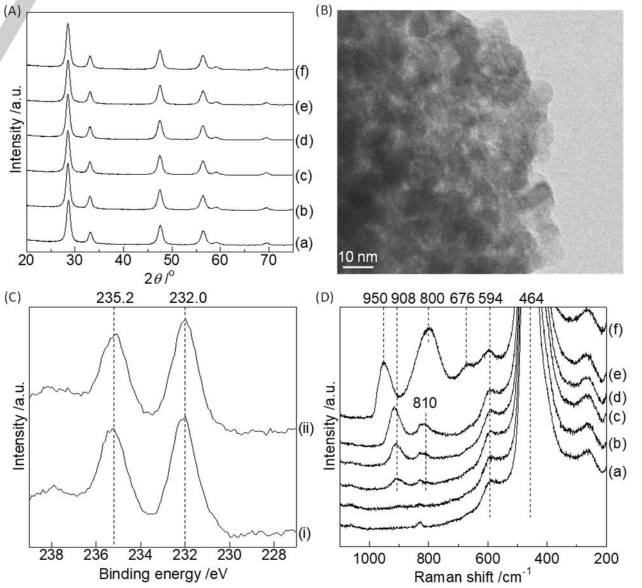

Figure 2. Characterization of MoO_x-CeO_2 and CeO_2. (A) XRD patterns of CeO_2 (a) and MoO_x-CeO_2 catalysts with different Mo loading amounts (b-f). (B) TEM image of MoO_x-CeO_2 (Mo: 1 wt%), (C) Mo 3d XPS of MoO_x-CeO_2 (Mo: 1 wt%) before (i) and after (ii) the reaction. (D) Raman spectra of CeO_2 (a) and MoO_x-CeO_2 catalysts with different Mo loading amounts (b-f). (a) 0 wt% (CeO_2), (b) 0.1 wt%, (c) 0.5 wt%, (d) 1 wt%, (e) 2 wt%, (f) 4 wt%).

particles for MoO_x species. This result agrees well with the results of XRD analyses. In order to clarify the state of MoO_x species on MoO_x-CeO_2 catalysts, XPS and Raman analyses were conducted. Mo 3d XPS of MoO_x-CeO_2 (Mo: 1 wt%) before and after the reaction showed two main signals at 232 and 235 eV (Figure 2 (C)), which are assigned to Mo^{6+} species. These signals were not changed before and after the reaction, suggesting that the valence of MoO_x species was not changed during the reaction. The Raman spectra of MoO_x-CeO_2 catalysts with different Mo loading amounts are shown in Figure 2(D). The bands at 460 and 595 cm^{-1} can be assigned to F_{2g} vibration mode of fluorite structure of CeO_2 and the oxygen vacancies, respectively and the intensity ratio was not changed, suggesting that the bulk structure of CeO_2 was not changed by addition of MoO_x species. Focusing on the band due to MoO_x species, main signals around 908 and 810 cm^{-1} were detected below 1 wt% Mo loaded CeO_2 catalysts, which can be assigned to the isolated tetrahedral MoO_4^{2-} species.[11] The signal was shifted to higher wavenumber with increasing the Mo loading amount, and the bands around 950, 800 and 676 cm^{-1} can be assigned to the polymerized MoO_x clusters[11]. Therefore, MoO_x-CeO_2 (Mo: 1 wt%) has isolated tetrahedral MoO_4^{2-} species on CeO_2. Based on the result that the yield decreased with higher Mo loading amount than 1 wt% in MoO_x-CeO_2 catalysts (Figure 1), the isolated Mo^{6+} species is an important species and the interface between the isolated Mo species and CeO_2 is the main active site.

The time-courses of the reactions with MoO_x-CeO_2 (Mo: 1 wt%) and CeO_2 catalysts are shown in Figure 3. MoO_x-CeO_2 showed higher conversion than CeO_2. The conversions over MoO_x-CeO_2 and CeO_2 catalysts were levelled off at about 60% and 20%, respectively. XRD (Figure S1), BET (Figure S1) and XPS (Figure 2(C)) analyses of the used MoO_x-CeO_2 catalyst showed that the structure was not changed, and hence the active site on the surface of MoO_x-CeO_2 can be poisoned or covered by some organic compounds during the reaction. TG-DTA analyses of MoO_x-CeO_2 and CeO_2 after 4 h reaction (Figure S2) showed an exothermic peak and the corresponding weight loss, and the weight loss over CeO_2 is about three times larger than that over MoO_x-CeO_2 catalyst. These results support that the active site was covered or poisoned by the deposited organic compounds. The reusability of MoO_x-CeO_2 was investigated (Figure S3). When the used catalyst was applied to the next reaction without calcination (only washing), the yield was drastically decreased by a factor of about three (53% to 17%). In contrast, the calcination treatment of the used catalyst at 573 K improved the catalyst reusability, and more than 35% conversion was maintained at fourth time reactions. These results also support that the active site of the catalyst was covered by the deposited organic compounds.

The MoO_x-CeO_2 amount was increased from 30 (standard) to 60, 90 and 120 mg to obtain a high yield of the target product (Figure 4(a), and the details are in Table S2). The conversion clearly increased with increasing the catalyst amount with high selectivity of >99%. In the case of 120 mg MoO_x/CeO_2 catalyst, 92 and 99% yields were obtained at 1 and 24 h, respectively.

To evaluate the reaction rate of MoO_x-CeO_2 and CeO_2 catalysts, the time-courses at low conversion level were measured with 120 mg MoO_x-CeO_2 and CeO_2 (Figure S4). The reaction rate, V (mmol min^{-1} g_{cat}^{-1}) was calculated by the following equation: V (mmol min^{-1} g_{cat}^{-1}) = (Formed target product (mmol))/ (Reaction time (min)) / (Catalyst amount (g)). The V of MoO_x-CeO_2 and CeO_2 was calculated to be 0.58 and 0.08 mmol min^{-1} g_{cat}^{-1}, respectively. Since the specific surface areas of CeO_2 (87 m^2 g^{-1}) and MoO_x-CeO_2 (85 m^2 g^{-1}) are similar, the activity contribution of Mo-based active sites of MoO_x-CeO_2 catalyst can be estimated to be at least 0.50 mmol min^{-1} g_{cat}^{-1} (0.58 – 0.08 mmol min^{-1} g_{cat}^{-1}). Considering that the main active site is the interface between isolated Mo species and CeO_2, the turnover frequency (TOF) based on the active site, namely Mo metal, is calculated to be 4.8 min^{-1}, and those based on CeO_2 and CeO_2 surface is estimated to be 0.014 and 0.065 h^{-1}, respectively (Figure 4(b) and Table S3).

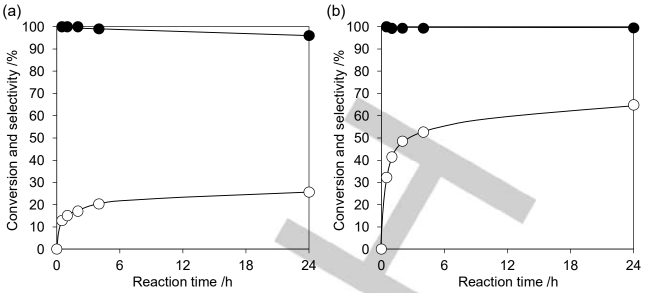

Figure 3. Time-courses of Michael addition reaction with CeO_2 (a) and MoO_x-CeO_2 (b) catalysts

Reaction conditions: 2-cyclohexen-1-one 1.0 mmol, dimethyl malonate 1.1 mmol, CeO_2 or MoO_x/CeO_2(Mo: 1 wt%) 30 mg, toluene 1.5 mL, 303 K, Ar. (○: Conversion, ●: Selectivity). Conversion and selectivity were based on 2-cyclohexen-1-one.

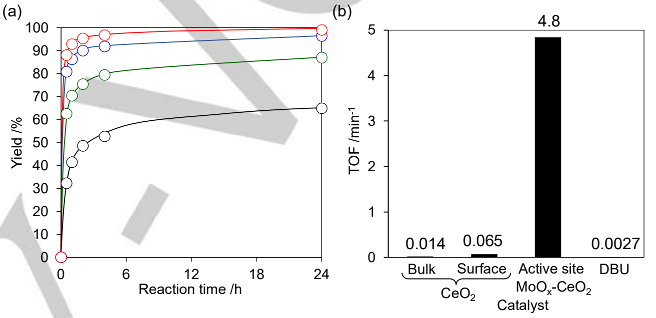

Figure 4 The catalyst amount effect on the performance of Michael addition reaction (a) and comparison of the activity of catalysts (b).

Reaction conditions of (a): 2-cyclohexen-1-one 1.0 mmol, dimethyl malonate 1.1 mmol, MoO_x-CeO_2(Mo: 1 wt%), toluene 1.5 mL, 303 K, Ar. (Black: 30 mg, green: 60 mg, blue: 90 mg, red: 120 mg). Yield was calculated on 2-cyclohexen-1-one basis. The TOFs (Table S3) were calculated from Figure S4 (Table S2) and Figure S5.

The activity of MoO_x-CeO_2 was compared with that of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), a strong organic base (pK_{aH}~24.3 in acetonitrile[12], Figure S5), which was reported to be effective for Michael reactions.[13] DBU showed activity with a little lower selectivity of ~96% than MoO_x-CeO_2, and the TOF of DBU is calculated to be 0.0027 min^{-1} (Figure 4(b) and Table S3). The TOF of the main active site over MoO_x-CeO_2 (4.8 min^{-1}) was 1800-fold higher than that of DBU. Considering that the basicity of the CeO_2 and MoO_x is lower than that of DBU, the acid-base bifunctionality of MoO_x-CeO_2 will play an important role in the reaction. CeO_2 is generally a basic metal oxide and the Lewis acidity of the Mo cation in MoO_x is higher than Ce cation in CeO_2 due to the higher oxidation state of Mo^{6+}. Therefore, CeO_2 will act as the Brønsted base for the activation of the C-H bond in the dimethyl malonate, and MoO_x will do as the Lewis acid site for the activation of the carbonyl group in 2-cyclohexen-1-one. The details of the reaction mechanism and catalysis are under investigation.

In conclusion, we found that MoO_x-modified CeO_2 (MoO_x-CeO_2) with 1 wt% Mo was an effective and reusable heterogeneous catalyst for Michael addition reaction, and the high yield (99%) of the target product was obtained. Based on the catalyst characterization results such as XRD, XPS, TEM and Raman, isolated Mo^{6+} species were formed on CeO_2 in MoO_x-CeO_2(Mo: 1 wt%) catalyst, and considering the experimental results, the active site of the catalyst is the interface between the isolated Mo^{6+} species and CeO_2. The activity based on the active site is 74-fold and 1800-fold higher than that of CeO_2 surface and a typical strong organic base of DBU.

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Keywords: Heterogeneous catalyst • Molybdenum oxide • Cerium oxide • Michael addition

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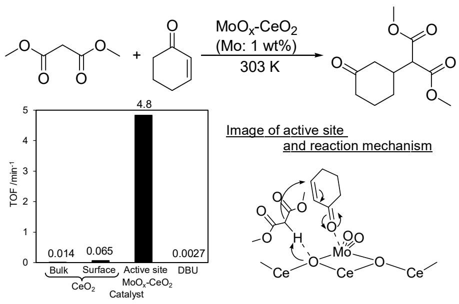

1wt% Mo loaded CeO_2 (MoO_x-CeO_2) catalyst was an efficient and reusable heterogeneous catalyst for the Michael addition of dimethyl malonate to 2-cyclohexene-1-one.