Catalytic Oxidation of Cyclohexene by Molecular Oxygen over Isopolyoxometalates

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Isopolyoxomolybdates exhibited high selectivities for the industrially useful products (cyclohexene oxide and 2-cyclohexen-1-ol) catalyzing effectively the reaction of initial product cyclohexenyl hydroperoxide with cyclohexene in the oxidation of cyclohexene by molecular oxygen.

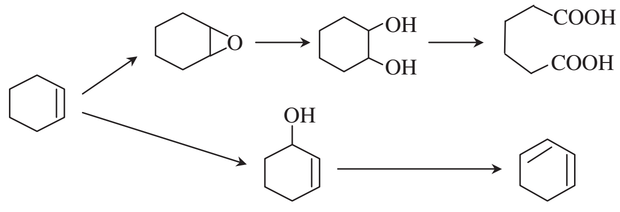
Polyoxometalates are polymeric oxoanions formed from one kind of polyanion (so-called isopolyoxometalates) or formed by condensation of more than two different mononuclear oxoanions (so-called heteropolyoxometalates).[1] Polyoxometalate catalysts are very attractive since they can effectively catalyze both acid and oxidation reactions in heterogeneous and homogeneous reaction systems.[2]

Because cyclohexene has been manufactured by the hydrogenation of benzene for the industrial preparation by Asahi Kasei Corporation,[3] the oxidation of cyclohexene to useful chemicals attracted a wide interest in industry.[4] Cyclohexene could be oxidized to cyclohexene oxide (denoted by Ch-O) or adipic acid using hydrogen peroxide as the oxidant.[5] Unfortunately, hydrogen peroxide is currently too expensive to allow an economically viable process. Molecular oxygen is the best oxidant due to low cost and significant advantages for environment. The main product of the cyclohexene oxidation by molecular oxygen without any reduction reagents reported in the literatures is 2-cyclohexen-1-one (denoted by Ch-one).[6] The only possible usage of Ch-one in industry is the hydrogenation of Ch-one to produce cyclohexanone. However, compared to the direct oxidation of cyclohexane to cyclohexanone, there is no economical benefit to produce cyclohexanone through oxidation of cyclohexene to Ch-one followed by hydrogenation of Ch-one. In this study, we wish to report that isopolyoxomolybdates exhibited high selectivities for the industrially useful products (Ch-O, 1,2-cyclohexanediol (denoted by Ch-diol) and 2-cyclohexen-1-ol (denoted by Ch-ol)) in the oxidation of cyclohexene by molecular oxygen.

Adipic acid is a necessary raw material for the manufacture of nylon-6,6. HNO_3 is used as the oxidant for the worldwide industrial adipic acid production and about 400000 metric tons of N_2O are emitted each year.[7] 1,3-Cyclohexadiene is widely applied in resin and perfumery industry.[8] We suggest a new route to manufacture adipic acid and 1,3-cyclohexadiene from the oxidation of cyclohexene as described in Scheme 1.

The main task in the new process is how to improve the yields of the industrially useful products (denoted by IUP, included Ch-ol, Ch-O, and Ch-diol) and impress the production of the industrially needless products in the cyclohexene oxidation using molecular oxygen as an oxidant.

Polyoxometalates were prepared according to the methods reported in the literatures.[6,9] The structures of the polyoxometalates synthesized in this study were confirmed by infrared spectroscopy and element analysis.

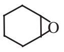
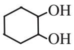
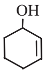
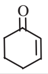
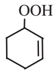
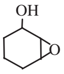


Scheme 1.

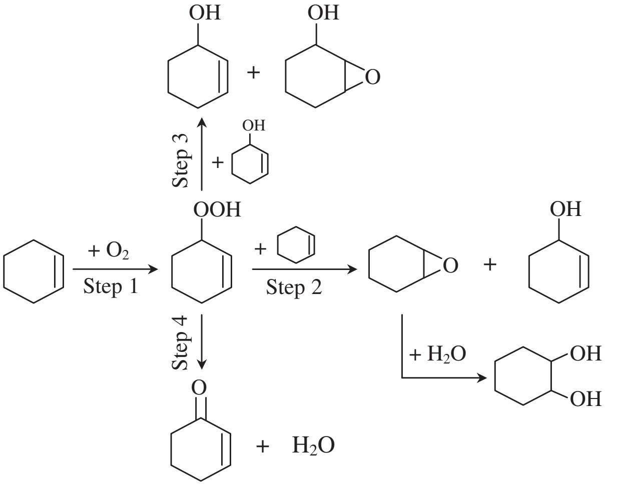
In a dry box, the catalyst (1.5 μmol) was added to a glass vial containing 1.5 mL of 1,2-dichloroethane, 0.1 mL of acetonitrile and a magnetic bar. Then freshly distilled cyclohexene (0.5 mL, 4.94 mmol) was added to the solution. The vial was sealed and attached to a vacuum line, cooled to 77 K (liquid N_2 bath), and 1 atm of O_2 was introduced to the system. After reacted under magnetic agitation, the reaction solution was analyzed by gas chromatography with a capillary column.

The conversion and product distribution over the various catalysts are shown in Table 1. The conversion of cyclohexene was 3.3% and the main product was cyclohexene hydroperoxide (denoted by CHHP) in the absence of a catalyst at 323 K for 24 h, which indicates that CHHP is the initial product in the oxidation of cyclohexene with molecular oxygen. The selectivities for IUP were 80.6, 90.1, and 82.3% over $(Bu_4N)_2Mo_2O_7$, $(Bu_4N)_2Mo_6O_{19}$, and $(Bu_4N)_4Mo_8O_{26}$ at the conversions of 31.8, 36.9, and 28.1%, respectively. These results indicated that isopolyoxomolybdates, especially $(Bu_4N)_2Mo_6O_{19}$, are suitable catalysts for the new process as described in Scheme 1. Isopolyoxotungstate $(Bu_4N)_2W_6O_{19}$ showed a high conversion of 52.7% but the selectivity for IUP was only 42.1%. The cyclohexene conversion and the selectivity for IUP were 30.5 and 63.6% over isopolyoxovanadate $(Bu_4N)_6V_{10}O_{28}$. As for the heteropolyoxometalates, $(Bu_4N)_3PMo_{12}O_{40}$, and $(Bu_4N)_3PW_{12}O_{40}$ showed low activities and low yields of IUP in the oxidation of cyclohexene with molecular oxygen. $(Bu_4N)_4PW_{11}Co(H_2O)O_{39}$, which is the most active polyoxometalate for the oxidation of cyclohexene with molecular oxygen reported in the literatures,[6] showed the highest conversion of 58.5% in this study but the selectivity for IUP was very low (31.1%). $(Bu_4N)_4PMo_{11}Ru(H_2O)O_{39}$ is the most selective catalyst for the formation of Ch-O and Ch-ol from the oxidation of cyclohexene with molecular oxygen reported in the literatures,[6] but it only showed a selectivity for IUP of 54.6% in this study, which was much lower than those of isopolyoxomolybdates in the oxidation of cyclohexene with molecular oxygen. As for the solvent effect, polyoxometalates showed high activities in 1,2-dichloroethane but the solubility of polyoxometalates in 1,2-dichloroethane is low. On the other hand, polyoxometalates easily solve in acetonitrile but the activities over polyoxometalates were low in acetonitrile. Thus we used 1,2-di-

Table 1. Oxidation of cyclohexene with molecular oxygen over various catalysts at 323 K[a]

Catalyst	Conversion /%	Selectivity/%						
								IUP[b]
Blank	3.3	2.4	0.5	6.1	6.4	84.5	0.2	9.0
$(Bu_4N)_2[Mo_2O_7]$	31.8	35.3	7.7	37.6	13.2	3.4	2.8	80.6
$(Bu_4N)_2[Mo_6O_{19}]$	36.9	40.2	8.3	41.6	4.7	3.8	1.4	90.1
$(Bu_4N)_4[Mo_8O_{26}]$	28.1	36.9	6.2	39.2	10.6	3.3	3.7	82.3
$(Bu_4N)_2[W_6O_{19}]$	52.7	20.7	2.8	18.6	38.6	11.4	7.9	42.1
$(Bu_4N)_3[PMo_{12}O_{40}]$	16.6	23.4	3.2	26.4	25.2	17.5	4.3	53.0
$(Bu_4N)_4[PW_{11}Co(H_2O)O_{39}]$	58.5	6.4	6.5	18.2	56.3	8.7	3.9	31.1
$(Bu_4N)_4[PMo_{11}Ru\ (H_2O)O_{39}]$	32.3	18.9	2.1	33.6	36.5	5.5	3.3	54.6

[a]Reaction conditions: catalyst, 1.5 µmol; 1,2-dichloroethane, 1.5 mL; acetonitrile, 0.1 mL; cyclohexene, 0.5 mL; $p_{O2} = 1$ atm; reaction time, 24 h. [b]IUP: industrially useful products, the sum of cyclohexene oxide, 1, 2-cyclohexenediol and 2-cyclohene-1-ol.



Scheme 2.

chloroethane/acetonitrile mixed solvents and the amount of acetonitrile was very low in this study.

The oxidation of cyclohexene with molecular oxygen initially forms CHHP as shown in Scheme 2 (Step 1). CHHP is not stable and can form Ch-O and Ch-ol by epoxidation of cyclohexene (Step 2), form 2,3-epoxycyclohexanol by reacting with Ch-ol (Step 3), or decompose to Ch-one and water (Step 4). The conversion of cyclohexene is controlled by the rate of Step 1 in Scheme 2 and the selectivity for IUP is controlled by the rate ratio of Step 2 to Step 3 and Step 4. $(Bu_4N)_2W_6O_{19}$ and $(Bu_4N)_4PW_{11}Co(H_2O)O_{39}$ showed high conversions in the oxidation of cyclohexene, which indicated that they effectively catalyzed Step 1 in Scheme 2. However, they did not effectively catalyze Step 2 in Scheme 2. The formed CHHP exists in the system for a long time and forms the undesirable products (Step 3 and Step 4 in Scheme 2). $(Bu_4N)_4PMo_{11}Ru(H_2O)O_{39}$ is a bifunctional catalyst which simultaneously catalyzes Step 1 and Step 2 in Scheme 2.[6b] It showed higher selectivity for IUP than those of $(Bu_4N)_2W_6O_{19}$ and $(Bu_4N)_4PW_{11}Co(H_2O)O_{39}$. Isopolyoxomolybdates catalyzed the Step 1 in Scheme 2 since the cyclohexene conversions over isopolyoxomolybdates were much higher than that of blank (without a catalyst). Moreover, isopolyoxomolybdates showed high selectivities for Ch-O and Ch-ol, which indicates that isopolyoxomolybdates extremely effectively catalyzed Step 2 in Scheme 2 and the rate of Step 2 was much faster than the rates of other steps. Once CHHP formed, it converts to Ch-O and Ch-ol very quickly over isopolyoxomolybdates. The selectivity for Ch-O (including Ch-diol) was lower than 50% over every catalyst in this study (Table 1), which indicates that Ch-O was produced as described in Step 2 in Scheme 2 with forming the same amount of Ch-ol. The contribution of the direct cyclohexene epoxidation by molecular oxygen is very small over isopolyoxomolybdates since the direct epoxidation of alkene by molecular oxygen would produce epoxide in high selectivity.

The used $(Bu_4N)_2Mo_6O_{19}$ catalyst was obtained by vacuum distillation of the mixture after reaction. The conversion and the selectivity for IUP did not decrease after reused for two times. These results indicate that $(Bu_4N)_2Mo_6O_{19}$ is reusable in the oxidation of cyclohexene by molecular oxygen.

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