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Epoxidation of β-ionone using molecular oxygen over Pt/MCM-41 catalyst under mild conditions

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The epoxidation of β-ionone over the Pt/MCM-41 catalyst using molecular oxygen in the liquid phase had been studied. The results indicated that the β-ionone was catalytically oxidized to 5,6-epoxy-β-ionone, 4-oxo-β-ionone, 4-hydroxy-β-ionone and dihydroactinidiolide using molecular oxygen as the sole oxidant. The effects of solvent, content of Pt, reaction temperature and time on the catalytic activity and product selectivity had also been investigated in detail.

KEY WORDS: β-ionone; epoxidation; platinum; MCM-41.

1. Introduction

The introduction of a functional group into terpenoids and steroids is an important reaction in synthetic chemistry. Many studies have been reported on the specific oxidation and reduction of olefins and alicyclic hydrocarbons with chemical reagents [1–3]. Epoxidation of olefinic compounds to corresponding epoxides is an important and first step in the production of large number of bulk, fine and pharmaceutical grade chemicals [1]. Compounds containing the 2,6,6-trimethylcyclohexane structural unit are of great importance in caroteniod chemistry and in the chemistry of fragrances and aromas, and it is a further object of the invention to increase the synthesis possibilities in these fields by providing novel intermediates [4]. 5,6-Epoxy-β-ionone has been used as a model metabolite and shown to be a more effective inhibitor of TPA action *in vitro* than β-ionone. This substance also presents an interest for the flavoring industry. Hirao *et al.* [5] have observed that the β-ionone could be oxidation with $VO(OR)Cl_2$ in alcohol to gain mainly allylic oxidation product, 4-oxo-β-ionone. Unfortunately, a large amount of $VO(OR)Cl_2$ must be used and the yield is low. Using sodium chlorate and sodium iodide as catalysts, β-ionone can be oxidized to 4-oxo-β-ionone [6]. However, the process need a large amount of catalysts and the process is complex.

MCM-41, a new member of the zeolite family, shows a regular hexagonal array of uniform pore openings with pore dimensions between 1.5 and 10 nm [7,8]. Because it has high thermal stability, high BET surface areas and large pore volumes, MCM-41 has already attracted considerable interest in recent years. It has been studied as catalyst, support and sorbent [9]. Pt catalysts based on porous materials are increasing important, primarily owing to their potential applications in industrially important chemical reactions and environmental protection. Recently, mesoporous MCM-41 materials have been used as supports for Pt [10–14]. However, this has not been sufficiently explored for the epoxidation of β-ionone. Here, we investigated the activity of Pt/MCM-41 in epoxidation of β-ionone with molecular oxygen as the sole oxidant under mild conditions. The effect of platinum content, solvent, reaction time and reaction temperature were studied in detail.

2. Experimental

Platinum supporting MCM-41 mesoporous molecular sieve was synthesized by a novel "$S^+X^-I^+$"(where S^+ was the surfactant; X^- was the Cl^-, Br^-, NO_3^-; and I^+ was the silicate) self-assembly process as following: 6.0 g of hexadecylpyridinium bromide (CPBr) were combined with 64 ml of HCl (5 M). When the mixture became clear under vigorous stirring, 12.4 g of tetraethylorthosilicate (TEOS) was added and then the solution of H_2PtCl_6 was introduced, under vigorous stirring to give a mixture with reactant composition (molar ratios) of 1 TEOS:0–0.25 H_2PtCl_6:0.3 CPBr:6 HCl:60 H_2O. After allowing the resulting gel to age at 328 K under gentle stirring for 24 h, the solid product was filtered, washed with de-ionized water, and air dried overnight, and then calcined in air at 873 K for 4 h to

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remove the template. According to the different platinum loading on the MCM-41, the catalysts were labeled as A–D. Pt/SiO_2 and Pt/ZSM-5 catalysts with Pt loading of 0.9 wt% were prepared by impregnation method using aqueous solution of hexachloroplatinic acid and starting materials SiO_2 and ZSM-5, respectively. The physical properties of the catalysts were confirmed by XRD, N_2 adsorption/desorption, and ICP-AES.

The oxidation of *β*-ionone was carried out in an autoclave using molecular oxygen as the sole oxidant over Pt/MCM-41 catalyst. Catalytic reaction of *β*-ionone oxidation was accomplished in an autoclave using 1.0 ml of *β*-ionone and 1.0 ml solvent. After reaction, the reactants and products were analyzed using a gas chromatograph (P. E. Auto System XL) fitted with a SE-30 column and a flame ionization detector (FID). They were further confirmed using a combined gas chromatography-mass spectrometry (GC-MS Agilent 6890/5973). A blank oxidation reaction of *β*-ionone over Si-MCM-41 in oxygen was also carried out under the same reaction conditions.

3. Results and discussion

The X-ray diffraction (XRD) analysis of dried samples of platinum/MCM-41 catalysts showed that the diffraction patterns of all the samples were similar with no indication of any peak corresponding to the oxides of platinum. The absence of any crystallites in our study suggests that a large number of highly dispersed smaller crystallites of PtO_2 may be present on the surface or inside the channel, which are not sufficiently large enough to be detected by XRD technique.

The chemical composition, the BET surface area and the pore volume of the samples were shown in table 1. The loadings of platinum had the modest effect on the surface area of the support and the pore diameter. The decreased of the volume cell was observed from the table 1 for the Pt/MCM-41 samples compared with the MCM-41 sample, suggesting that Pt, as expected due to its big cluster volume, did not isomorphously substitute the Si^{4+} in framework position, but entered into the channel or deposited on the external surface of the crystal.

The catalytic performance of 0.9–4.6% Pt/MCM-41 for the oxidation of *β*-ionone with molecular oxygen as the sole oxidant in chloroform was shown in table 2. The products obtained were 5,6-epoxy-*β*-ionone (**2a**), 4-oxo-*β*-ionone (**3a**), 4-hydroxy-*β*-ionone (**4a**) and dihydroactinidiolide (**5a**), which had been defined in figure 1. The conversion of *β*-ionone and the selectivity of 5,6-epoxy-*β*-ionone were up to 98% and 80%, respectively. To the best of our knowledge, it was the first time to report such excellent conversion and selectivity for *β*-ionone epoxidation under such mild reaction system. It can be seen from the

Table 1
ICP-AES data and BET surface area of various Pt/MCM-41

Catalyst	Pt content (wt%)	d_{100} (Å)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
MCM-41	–	34.4	1089	0.66	3.6
A	0.90	37.2	922	0.99	4.3
B	1.78	36.8	1023	0.89	3.5
C	2.93	35.6	1206	0.84	2.8
D	4.59	34.8	1176	0.79	2.7

Table 2
Results of *β*-ionone epoxidation over different Pt catalyst[a]

Catalyst	Pt content (wt%)	Conversion (%)	Selectivity (%)			
			2a[b]	**3a**[c]	**4a**[d]	**5a**[e]
MCM-41	–	10.3	76.5	17.7	5.3	0.5
Pt/SiO_2	0.90	50.7	75.1	15.2	8.7	1.0
Pt/ZSM-5	0.90	67.3	73.4	16.8	8.7	1.1
A	0.90	97.5	80.5	11.3	7.3	0.9
B	1.78	98.6	73.5	16.5	8.8	1.2
C	2.93	99.0	72.8	16.0	9.7	1.5
D	4.59	98.7	74.1	14.1	10.1	1.7

[a] Reaction condition: *β*-ionone 1.0 ml; solvent trichloromethane 1.0 ml; catalyst 50 mg; O_2 1.0 MPa; reaction temperature 353 K; reaction time 22 h; stirrer.

[b] **2a** 5,6-epoxy-*β*-ionone; [c] **3a** 4-oxo-*β*-ionone; [d] **4a** 4-hydroxy-*β*-ionone; [e] **5a** dihydroactinidiolide.

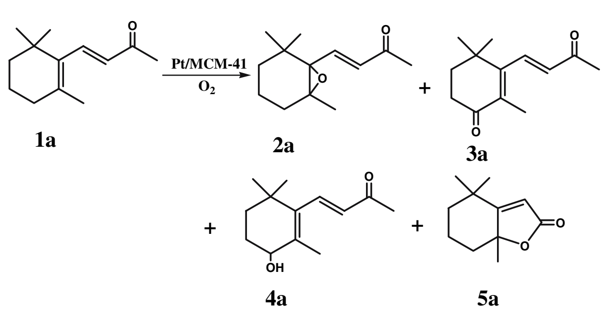

Figure 1. Main products formed in the oxidation of β-ionone.

table 2 that Pt content had a little effect on the conversion of β-ionone, while the selectivity of 5,6-epoxy-β-ionone was found to decrease with the increase of Pt content. Compared with Pt/ZSM-5 and Pt/SiO$_2$ catalysts, it can be found that the Pt/MCM-41 catalyst has the best activity. This indicated that the nature of the support plays an important role in the activity of oxidation of β-ionone. The high activity obtained on the Pt/MCM-41 catalysts was likely due to the large pores and high surface area of MCM-41.

The effect of solvent on oxidation of β-ionone over 0.9% Pt/MCM-41 at 333 K was studied. Reactions were carried out with both polar and non-polar solvents (table 3) and catalytic activity was analyzed based on the dielectric constant (ε) and electron donor number (DN) of solvent. The DN is a dimensionless and more accurate polarity scale [15,16], directly related to the trend toward complex formation with a metal center, which can retard or avoid the formation of oxo metal complex (active oxidation species) [17]. As can be observed in table 3, the conversion of β-ionone increased as ε decreased and, in general, DN decreased. Although the lowest conversion of β-ionone was expected with acetonitrile (entry 3) due to its high ε value, its low DN value appears to be also important. So, the solvent played an important role in tuning the performances of catalysts due to the dielectric constant (ε) and electron donor number (DN), and the catalyst had an optimum activity using chloroform as the solvent.

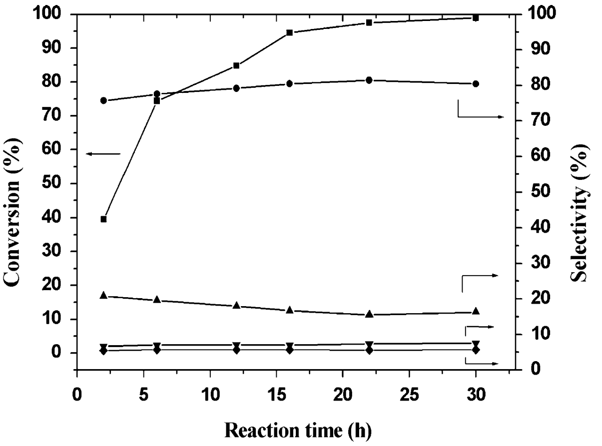

Figure 2. Effect of reaction time on the conversion and selectivity over Pt/MCM-41 (■ β-ionone conversion; ● 5,6-epoxy-β-ionone selectivity; ▲ 4-oxo-β-ionone selectivity; ▼ 4-hydroxy-β-ionone selectivity; ◆ dihydroactinidiolide selectivity).

The effect of reaction time on oxidation of β-ionone over 0.9% Pt/MCM-41 at 333 K was studied, and the results were shown in figure 2. It can be seen from the figure that the conversion of β-ionone increased with the prolonging of the reaction time, and the selectivity of 5,6-epoxy-β-ionone increased at first, passing through a maximum at 22 h, and then decreased.

The influence of reaction temperature on oxidation of β-ionone over 0.9% Pt/MCM-41 was also investigated, and the results were shown in figure 3. As shown in figure 3, the conversion of β-ionone increased with increasing reaction temperature. However, with increasing temperature, the selectivity of 5,6-epoxy-β-ionone increased at first, passing through a maximum at 333 K, and then decreased at 343 K.

Recycling tests with repeated use of 0.9% Pt/MCM-41 in four consecutive reactions were carried out. The catalyst was removed from the reaction system after 22 h by filtration, washed with acetone, dried at 393 K for 5 h and subjected to the next catalytic run under the same reaction conditions. Figure 4 illustrated that Pt/MCM-41 could be recycled three times without obviously activity loosing. A slight decrease in the conversion of

Table 3

Epoxidation of β-ionone over Pt/MCM-41 (0.9%) catalyst using various solvents[a]

Entry	Solvent	Dielectric constants (ε)	Electron donor numbers (DN)	Conversion (%)	Selectivity (%)			
					2a[b]	**3a**[c]	**4a**[d]	**5a**[e]
1	Methanol	32.6	30.0	73.5	70.2	19.2	8.2	2.4
2	Ethanol	24.3	32.0	80.9	67.9	22.0	9.0	1.1
3	Acetonitrile	37.5	14.1	89.8	66.4	22.9	9.9	0.9
4	Acetone	20.7	17	92.1	67.1	21.7	11.0	0.8
5	Ethyl acetate	6.02	17.1	96.6	70.0	20.1	9.0	2.4
6	Trichloromethane	4.806	4.0	97.5	80.5	11.3	7.3	0.9

[a] Reaction condition: β-ionone 1.0 ml; solvent 1.0 ml; catalyst 50 mg; O_2 1.0 MPa; reaction temperature 353 K; reaction time 22 h; stirrer.
[b] **2a** 5,6-epoxy-β-ionone; [c] **3a** 4-oxo-β-ionone; [d] **4a** 4-hydroxy-β-ionone; [e] **5a** dihydroactinidiolide.

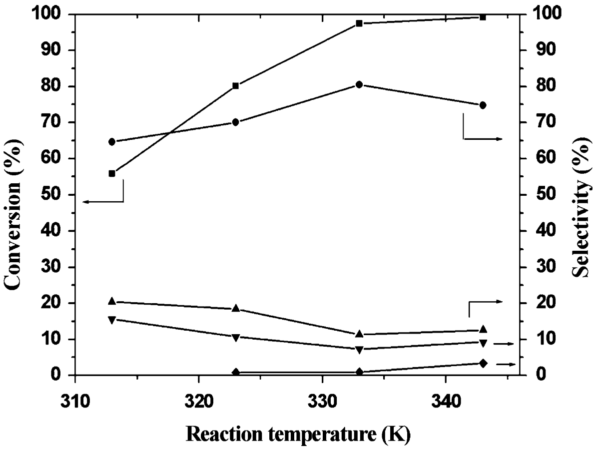

Figure 3. Effect of reaction temperature on the conversion and selectivity over Pt/MCM-41. (■ β-ionone conversion; ● 5,6-epoxy-β-ionone selectivity; ▲ 4-oxo-β-ionone selectivity; ▼ 4-hydroxy-β-ionone selectivity; ◆ dihydroactinidiolide selectivity).

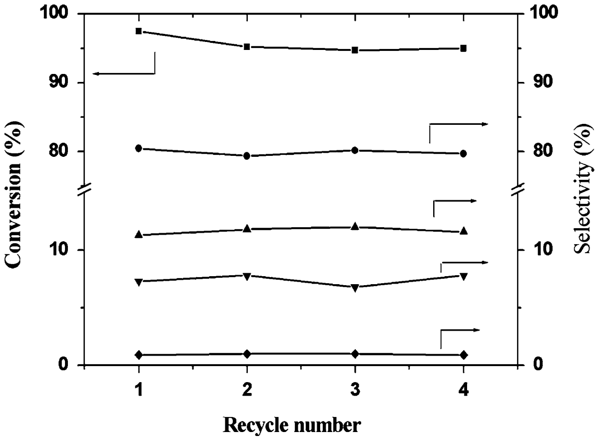

Figure 4. Results of catalyst reused four times over Pt/MCM-41. (■ β-ionone conversion; ● 5,6-epoxy-β-ionone selectivity; ▲ 4-oxo-β-ionone selectivity; ▼ 4-hydroxy-β-ionone selectivity; ◆ dihydroactinidiolide selectivity).

β-ionone could be due to loss of some catalyst during filtration and no addition of any fresh catalyst to keep the amount of catalyst used the same.

4. Conclusions

In summary, a calcined Pt/MCM-41 catalyst is found to be very efficient for the epoxidation of β-ionone using molecular oxygen as the sole oxidant under mild conditions. The catalyst can be used repeatedly for at least three times without any obviously loss of catalytic activity.

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