Catalytic aerobic epoxidation of olefins by nanostructured amorphous CoO–MCM-41

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Nanostructured amorphous cobalt oxide deposited inside the pores of MCM-41 using ultrasonic deposition–precipitation of cobalt tricarbonyl nitrosyl in decalin was found to be an efficient catalyst for the epoxidation of olefins under aerobic conditions.

KEY WORDS: epoxidation; olefins; cobalt oxide; MCM-41; deposition–precipitation.

1. Introduction

Epoxidation of olefins using molecular oxygen in the presence of transition metal catalysts has attracted much interest in recent years. The process is valuable both economically and environmentally. Most of the earlier methods of direct epoxidation using molecular oxygen have involved specially designed transition metal complexes. The search is still ongoing for catalysts which are designer simple and heterogeneous for easy product separation and catalyst recovery. There are recent reports where nickel acetylacetonate [1] and cobalt salen complexes [2] supported on organic polymers have been used as catalysts for alkene epoxidation under aerobic conditions. The polymer-bound complex acts as a heterogeneous catalyst and can be removed from the reaction mixture with partial loss of activity due to leaching.

Since its discovery in 1992, the M41S family in general, and MCM-41 in particular, have attracted much attention owing to their large surface area [3]. Various methods have been applied to deposit a monolayer of various catalysts on its surface. The most popular method is impregnation [4], but other methods such as gas-phase deposition [5], ion exchange and the direct addition of the catalytic ion to the gel [6] have also been employed. Cobalt was frequently loaded into the pores of MCM-41 as the sole ion [7].

The concept of using sonochemical methods both for the preparation of mesoporous materials and for the deposition of catalysts into the mesopores was described recently [8]. It is already well documented that when ultrasound radiation passes through a decalin solution of a transition metal (TM) carbonyl, it yields a powder containing amorphous nanoparticles [9]. If the irradiation is carried out under argon, nanophased, amorphous, zerovalent transition metals are obtained [9,10]. On the other hand, if sonication is conducted under air, a nanophased amorphous transition metal oxide is the product of sonication [11]. Ultrasonication of a slurry containing a metal carbonyl and a high-surface-area silica-based mesoporous material (MCM-41) results in the deposition–precipitation of the corresponding metal oxide, forming a close-packed monolayer on the surface [12]. This is a result of ultrasonically-induced chemical interaction between the metal oxide and the surface silica atomic layer, yielding surface silicates.

Here, we report the epoxidation of alkenes using molecular oxygen in the presence of isobutyraldehyde as a sacrificial reductant and nanostructured amorphous cobalt oxide–mesoporous silica (MCM-41) composite as a catalyst. This method is simple in terms of facile reactivity, moderate regioselectivity and stereoselectivity and reusability of the catalyst.

2. Experimental

2.1. Preparation of the catalyst

The mesoporous silica (MCM-41) was prepared sonochemically [13]. Sonochemical deposition of amorphous cobalt oxide was carried out as follows: 1 g of MCM-41 was added to 90 ml of dry decalin in a sonication cell, and the cell was attached to the sonicator horn under a flow of argon. Argon was bubbled through the slurry for 30 min prior to the sonication to expel any dissolved air or oxygen. Cobalt tricarbonyl nitrosyl (Strem Chemicals) (0.27 ml) was introduced into the slurry through a septum (the planned concentration of cobalt oxide on MCM-41 is 16%). Because of the very

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high sensitivity of $Co(CO)_3NO$ to oxygen, the syringe used for the transfer of cobalt tricarbonyl nitrosyl to the sonication cell was filled with argon. The sonication of the slurry was effected with high-intensity ultrasonic radiation employing a direct immersion titanium horn (Sonics and Materials VC-600 ultrasonic processor, 20 kHz, 120 W/cm^2) for 3 h. The temperature of the sonication process was kept at 90 °C. After the start of the sonication, the argon flow was discontinued and the sonication cell was exposed to ambient air. The resulting product after sonication was washed three times with anhydrous pentane in a centrifuge and dried under vacuum.

2.2. Characterization

Ultrasonic decomposition of the organometallic precursor $Co(CO)_3NO$ in the presence of MCM-41 and molecular oxygen at lower concentrations leads to the formation of a close-packed monolayer of CoO inside the pores. The deposited CoO is amorphous as no distinct peaks are observed in powder XRD and it is highly dispersed (TEM). The concentration of cobalt oxide is 13% as determined by SEM-EDAX at various regions of the sample. Increasing the loading of CoO leads to blocking of the pores. Further increase leads to crystallization of metal oxide particles outside the pores. The concentration of cobalt oxide is therefore critical. HR-TEM (high magnification) indicated that the thickness of the CoO monolayer inside the pores is 0.4 nm. Also, the ultrasonic decomposition of $Co(CO)_3NO$ does not cause any structural degradation of MCM-41 material as a hexagonal pore structure can still be detected (figure 1). The exposed surface area of the CoO–MCM-41 catalyst was determined as 800 m^2/g based on N_2 adsorption characteristics. Since ultrasonication leads to the formation of a close-packed monolayer of metal oxide inside the pores (without pore blocking), the reduction in surface area from parent MCM-41 is small [12]. Other deposition methods such as impregnation lead to a larger decrease in the surface area of mesoporous MCM-41 after deposition [12].

3. Catalytic reactions

A typical procedure is given for the epoxidation of β-ionone. To a stirred solution of **9** (192 mg, 1 mmol), isobutyraldehyde (0.27 ml, 3 mmol) and sodium hydrogencarbonate (252 mg, 3 mmol) in dry 1,2-dichloroethane (10 ml) was added CoO–MCM-41 (10 mg, 13% CoO content, 1.78 mol%). The reaction mixture was evacuated and stirred under 1 atm of oxygen at room temperature (28 °C). After completion of the reaction (3 h, TLC) the reaction mixture was filtered through a small pad of Celite and the filtrate was concentrated. The crude product was purified by chromatography on silica gel using 5% EtOAc–hexanes as eluent to yield epoxide **9a** as a pale yellow oil (165 mg, 81%).

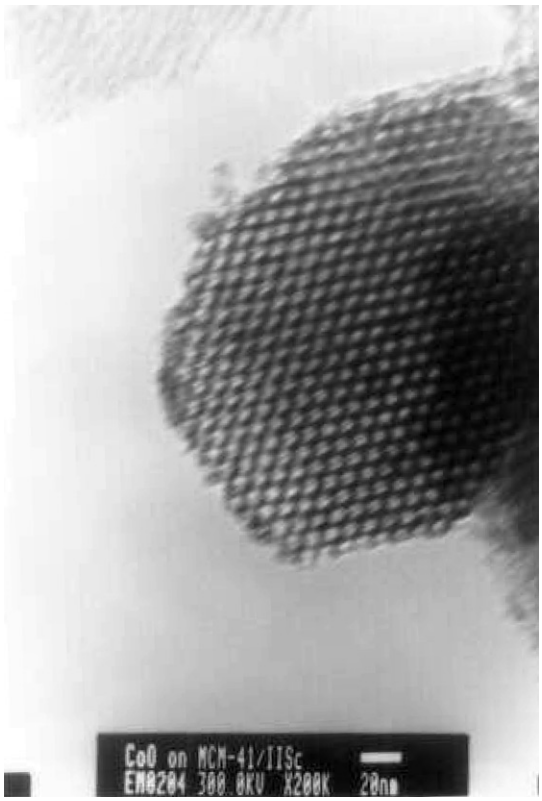


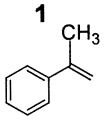
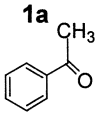
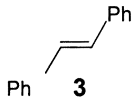
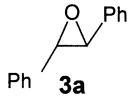
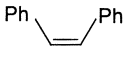
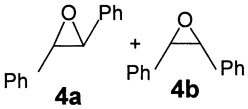
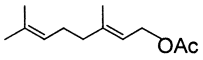
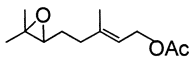
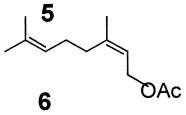
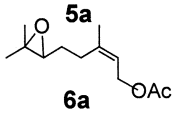
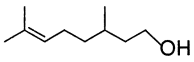
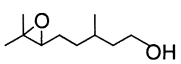
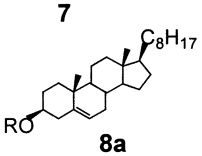
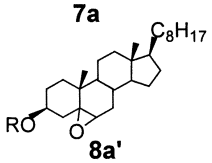
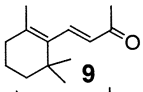
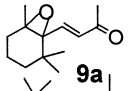
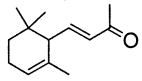
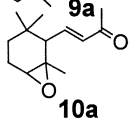
Figure 1. HR-TEM image of CoO–MCM-41.

4. Results and discussion

4.1. Catalytic epoxidation using CoO–MCM-41

Epoxidation of olefins was carried out using CoO–MCM-41 by employing aerobic oxidation in the presence of a sacrificial reductant such as isobutyraldehyde [14]. As summarized in table 1, the epoxidation reaction of simple olefins with CoO–MCM-41 catalyst was completed within a few hours (3–6 h). Whereas cyclooctene (**1**) was epoxidized to cyclooctene oxide (**1a**) in good yield, acetophenone (**2a**) was the major product from 2-methylstyrene (**2**) where oxidative cleavage has taken place. Oxidation of *trans*-stilbene (**3**) yielded *trans*-stilbene epoxide (**3a**) exclusively, whereas *cis*-stilbene (**4**) yielded a mixture of *cis*- and *trans*-epoxides (**4b** and **4a**) in a ratio of 1 : 3.6. Geranyl and neryl acetates (**5** and **6**) afforded the corresponding epoxides (**5a** and **6a**) in which the double bonds remote from the acetoxy groups were epoxidized with moderately high regioselectivity. It is noteworthy that in both cases the reaction was very fast, which is in sharp contrast to the longer reaction times needed using $Ni(dmp)_2$ as a catalyst [14]. In the case of citronellol (**7**), the corresponding epoxide (**7a**)

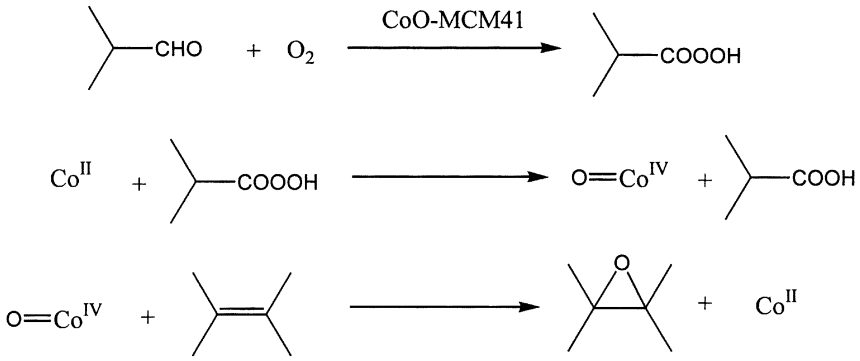
Table 1
Catalytic aerobic epoxidation of olefins using nanostructured CoO–MCM-41

Entry	Substrate	Time (h)	Product	TON	Yield (%)[a]	Selectivity
1	 **1**	3	 **1a**	53	95	
2	 **2**	3	 **2a**	50	90	
3	 **3**	3	 **3a**	50	90	
4	 **4**	4	 **4a** **4b**	51	92	*trans* : *cis* 3.6 : 1[b]
5	 **5**	4	 **5a**	34	61	
6	 **6**	4	 **6a**	31	56	
7	 **7**	5	 **7a**	32	58	
8	 **8a** **8b**	3 4	 **8a'** **8b'**	36 45	64 80	$\beta:\alpha$ (69 : 31)[b] (78 : 22)
9	 **9**	3	 **9a**	45	81	
10	 **10**	4	 **10a**	42	75	

[a] Isolated yield.
[b] Diastereomeric ratio determined by proton NMR integration.

was isolated in good yield and there was no oxidation of the primary alcoholic functionality.

Epoxidation of cholesterol (**8a**) and its esters proceeded smoothly with moderate diastereoselectivity. Cholesteryl acetate (**8b**) was epoxidized in high yields with preferential formation of 5,6-β-epoxide (**8b′**) ($\beta:\alpha = 78:22$). In the reaction of cholesterol (**8a**), the corresponding 5,6-β-epoxide (**8a′**) was the major product and there neither oxidation of the secondary alcohol nor isomerization of the double bond occurred. Epoxidation of α- and β-ionones (**9** and **10**) resulted in good yields of the epoxides (**9a** and **10a**) in which the non-conjugated double bond was epoxidized. The nanostructured CoO–MCM-41 catalyst was centrifuged after the reaction and could be reused successfully for a second run without appreciable loss of activity. In order to evaluate the possibility of leaching, the reaction mixture was filtered to remove the catalyst and cyclooctene was added to the filtrate. Although the filtrate did catalyze the epoxidation of cyclooctene, the conversion was only 10% after 6 h. The catalyst is not leached because the metal oxide is bonded to the substrate (MCM-41) by Co–O–Si bonds analogous to the MoO_x catalyst reported previously [12]. The hexagonal mesoporous



Scheme 1.

structure could still be detected in the recovered catalyst using HR-TEM.

4.2. Role of the sacrificial reductant and plausible mechanism for catalytic epoxidation

The role of isobutyraldehyde as a sacrificial reductant is similar to that suggested by Yamada *et al.* [14]. A plausible mechanism for catalytic epoxidation is outlined in scheme 1. The reaction of isobutyraldehyde with molecular oxygen in the presence of CoO–MCM-41 catalyst generates perisobutyric acid. This subsequently reacts with divalent cobalt (in CoO–MCM-41) to form a highly reactive oxo-cobalt(IV) intermediate similar to that proposed by Koola and Kochi [15]. Oxygen is transferred to the olefin by the oxo-cobalt(IV) intermediate with regeneration of the original metal oxide catalyst, which turns over to the next cycle.

The formation of perisobutyric acid is very slow and hence there is very little epoxidation in the absence of CoO–MCM-41 catalyst. Further, that the oxo-cobalt(IV) could be the oxygen transfer species and not perisobutyric acid is substantiated by the results obtained during aerobic epoxidation of Δ^5-unsaturated steroid derivatives (entry 8, table 1). While epoxidation of Δ^5-unsaturated steroids **8a** or **8b** with peracids provides the corresponding α-epoxides as the major product [16], aerobic epoxidation catalyzed by CoO–MCM-41 gives diastereoselectivity in favor of β-epoxides.

When catalytic epoxidation with CoO–MCM-41 was carried out in the presence of other oxidants such as hydrogen peroxide or *tert*-butyl hydroperoxide at room temperature, very poor conversions (10–15%) to the epoxide was observed.

In conclusion, ultrasonic decomposition of $Co(CO)_3NO$ in the presence of MCM-41 yielded a close-packed monolayer of cobalt oxide inside the pores. This CoO–MCM-41 composite catalyst was found to be efficient for the epoxidation of olefins under aerobic conditions. Further work on the catalytic activity of this catalyst is under investigation.

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