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Studies of catalytic aerobic oxidation with nanostructured amorphous metals, alloys and metal oxides[†]

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Abstract

The oxidation of cyclohexane with molecular oxygen in the presence of isobutyraldehyde catalyzed by nanostructured iron and cobalt oxides and iron oxide supported on titania has been studied. It was found that highly dispersed transition metal oxide is more effective for oxidation than the corresponding zero-valent metal powders. Nanostructured cobalt oxide on MCM-41 is found to be efficient for catalytic aerobic epoxidation of olefins. The catalyst is reusable and gives moderate to high regio- and stereoselectivity.

Keywords: Nanostructures, catalysts, aerobic oxidation, alkanes, alkenes.

1. Introduction

The functionalization of inactivated carbon–hydrogen bonds in saturated hydrocarbons has been investigated for both synthetic and biological interest [1]. Direct attack of oxygen on cyclohexane is an endothermic process. Various oxidants have been explored and alternative sources of active oxygen such as iodosobenzene [2], hydrogen peroxide [3], alkylhydroperoxide [4] are used instead of energy-consuming dioxygen activation. Barton *et al.*[5a] have developed a new system referred to as Gif system that allows the oxidation of saturated hydrocarbons under mild conditions (ambient temperature, atmospheric pressure and nearly neutral pH). It involves the use of iron (II) salt, zinc powder and oxygen (air) and has been shown to give 20% conversion in the oxidation of cyclohexane to a mixture of cyclohexanone and cyclohexanol [5]. To facilitate the isolation of reaction products, a new Gif–KRICT system was developed in which the active iron catalyst was bound to the solid support [6]. However, the conversion of cyclohexane to products was lower (5–7 %) than that observed for the original Gif system [7]. Murahashi *et al.* carried out the oxidation of cyclohexane with iron powder and obtained 11% conversion and 95% selectivity for cyclohexanol and cyclohexanone under mild conditions (1 atm O_2, room temperature, 15h) [8].

It is to be expected that the use of nanostructured catalysts will enhance the catalytic activity due to increase in surface area. However, the superiority of nanoamorphous over nanocrystlline catalysts was demonstrated only recently [9]. Due to a very high cooling rate under sonochemical conditions, volatile precursors always lead to nanoparticles.

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2. Studies on cycloalkane oxidation with nanostructued amorphous metals and alloys

Suslick and coworkers demonstrated the first sonochemical synthesis of amorphous iron particles (10–20 nm) by ultrasonic irradiation of $Fe(CO)_5$ and its utility as efficient catalyst in Fischer–Tropsch process [9]. They have extended the sonication synthesis to nanostructured amorphous cobalt (20 nm) and an amorphous Co/Fe alloy [10]. Earlier, we had described the sonochemical synthesis of amorphous nickel [11] (10 nm) from $Ni(CO)_4$ and amorphous Fe/Ni alloy [12] ($Fe_{20}Ni_{80}$, 25 nm) from a solution of $Fe(CO)_5$ and $Ni(CO)_4$.

The amorphous nature and the particle size were established by XRD and TEM measurements respectively [13].

We have reported recently on the efficacy of using nanostructured amorphous metals like Fe and Co and amorphous alloy like $Fe_{20}Ni_{80}$ with oxygen (40 atm) at room temperature (25–28^{o}C) for the oxidation of cyclohexane with up to 40% conversion with 80% selectivity [14] for cyclohexanone and cyclohexanol. In cyclohexane oxidation, use of amorphous cobalt gave the best result at 41% conversion and 80% selectivity for cyclohexanone and cyclohexanol. In a control reaction where the same cycloalkanes were reacted with molecular oxygen, isobutyraldehyde and acetic acid, no oxidation products were obtained in the absence of amorphous Co, Fe or alloy as catalysts. When the oxidation of cyclohexane was carried out using nanostructured Co (20 nm) catalyst at 70^{o}C under 40 atm of oxygen for 8 h, it was found that the conversion had gone up to 67% but there was a change in the ratio of ketone: alcohol (1:2). Oxidation of adamantane with various nanometal/alloys was carried out under similar conditions [28^{o} C, O_2 (40 atm)] and in general the conversion was in the range of 52–57% and adamantan-1-ol was the major product in all the reactions. Interestingly, no other oxidation products were observed in our reaction (100% selectivity).

The reaction can be rationalized by assuming the following pathway similar to that suggested by Murahashi *et al.* [8]. The reaction of isobutyraldehyde with molecular oxygen in the presence of amorphous metal/alloy and acetic acid would give perisobutyric acid, which subsequently reacts with metal/alloy to form oxometal species. Abstraction of hydrogen atom from cyclohexane followed by hydroxy ligand transfer to the resulting radical would give the product. In the course of these studies, we suspected that the highly reactive amorphous iron and cobalt nanoparticles would undergo ready oxidation and, in fact, the corresponding oxides may be the actual catalysts in our hydrocarbon oxidations. To check this hypothesis and to extend the catalytic studies to include iron oxide supported on titania, further work was undertaken.

3. Oxidation of cyclohexane with nanostructured amorphous transition metal oxides as catalysts

The metal oxide catalysts were prepared by ultrasonic irradiation as per the procedure described earlier [15]. Unlike the sonication of transition metal carbonyls under argon which yields the corresponding metals, sonication under air yields transition metal oxides. Thus sonication of 1 M solution of iron pentacarbonyl or cobalt (III) carbonylnitrosyl in decalin in the presence of oxygen at 0^{o}C for 3 h resulted in the formation of the corresponding nanostructured metal oxide. The supported iron oxide/titania catalysts were prepared by the sonication of titanium oxide powder (Degussa P25, surface area 45 m^2/g) with iron pentacarbonyl in decalin at 0^{o}C for 3 h.

The structure and particle size of the catalysts were established by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The particle size of the titania-supported catalyst, measured by TEM, was about 40 nm. It was coated with highly dispersed nanoparticles of 5–10 nm of iron oxide. The size of the iron oxide obtained from the sonication of 1 M iron pentacarbonyl (in the absence of titania) was 8–10 nm and 4–6 nm from 0.5 M.

When sonochemically prepared iron oxide was used as a catalyst for the oxidation of cyclohexane with oxygen (1 atm) at 70ºC, cyclohexanol and cyclohexanone were obtained (16.5% conversion, 90% selectivity). The ratio of cyclohexanol to cyclohexanone (ol : one) was about 1.5 : 1. It turns out that the amorphous catalyst is the only active form of iron oxide which could react with perisobutyric acid and form the oxometal species for cyclohexane oxidation. With amorphous cobalt oxide (Co_3O_4) as a catalyst, a conversion of 4–5% of cyclohexane was achieved. It is well known that titanium oxide is an efficient oxygen activator and at the same time it can be used as a carrier for transition metal catalysts by promoting their stability and reactivity due to metal-support interaction [16]. We have employed the sonication method to anchor the nanostructured amorphous iron oxide on the titania surface and studied the activity of as-prepared catalyst in the oxidation of cyclohexane. (Table I). The conversion percentage of the initial product on supported iron oxide/titania catalyst was higher than that on unsupported amorphous iron oxide. A control reaction in which titania was used as the catalyst for the oxidation showed that titania itself was not effective in the cyclohexane oxidation. Its functions are, therefore, the stabilization and activation of iron oxide. The activity of iron oxide–titania catalyst also depend on the conditions of preparation.

4. Mesoporous iron–titania catalyst for cyclohexane oxidation

Synthesis of mesoporous materials offers a new possibility for the creation of catalysts that are effective in many industrial processes. The mesoporous titanium oxide was synthesized from titanium isopropoxide by ultrasound irradiation [17]. Its surface area, measured by the BET nitrogen adsorption method after removal of the surfactant, reached 850 m^2/g, with a pore size of 1.5 nm and a pore volume of 0.53 ml/g. A mixture of titania prepared this way and iron pentacarbonyl in decalin was irradiated by ultrasound under an atmospheric pressure of air at 0ºC for 3 h. The surface area of the sample was 570 m^2/g, with a pore size of 1.3 nm and a pore volume of 0.23 ml/g.

We have studied the reaction of cyclohexane oxidation with iron oxide supported on mesoporous titania under mild conditions (O_2, 1 atm; 70ºC). This showed the highest activity in the cyclohexane oxidation (selectivity almost 90% and conversion 26%) (Table I). We believe

Table I
Aerobic oxidation of cyclohexane using highly dispersed transition metal oxides (1 atm O_2)

Catalyst	Particle size (nm)	Temp.(ºC)	Conversion (%)	ol:one
Fe_2O_3	8-10	70	16.5	1.5 : 1
Co_3O_4	10	70	4.8	1.6 : 1
Fe_2O_3/TiO_2	30	70	21.3	1.1 : 1
Fe_2O_3/TiO_2 (Mesoporous)		70	26	1.5 : 1

that the sonochemically prepared iron oxide deposited on mesoporous titania is indeed a homogeneous–heterogeneous system fabricating the active oxometal complexes during the reaction.

5. Nanostructured cobalt oxide supported on MCM-41: A versatile catalyst for epoxidation of olefins under aerobic conditions

Epoxidation of olefins using molecular oxygen in the presence of transition metal catalysts has attracted considerable interest in recent years. Most of the earlier methods of direct epoxidation using molecular oxygen have involved specially designed transition metal complexes. Search is still on for catalysts which are simple to design and heterogeneous for easy product separation and catalyst recovery. Herein, we report the epoxidation of alkene using molecular oxygen in the presence of an aldehyde and nanostructured cobalt oxide supported on mesoporous silica (MCM-41). This method is simple in terms of easier reactivity, moderate regio- and stereo selectivity as well as reusability of the catalyst.

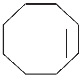
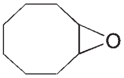
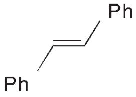
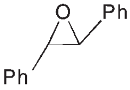
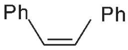
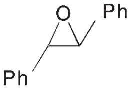
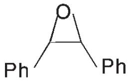
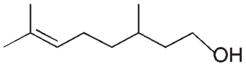
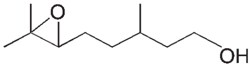
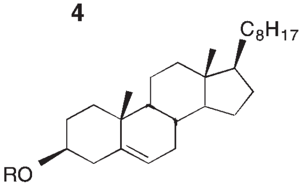
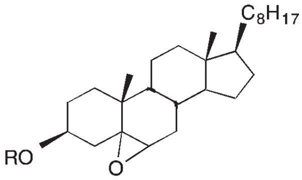
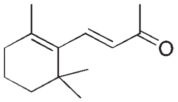
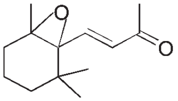
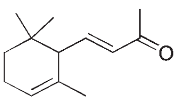
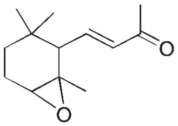
Since its discovery in 1992, the M41S family in general and MCM-41 in particular, have attracted much attention due to their large surface area [18]. Various methods have been applied to deposit a monolayer of various catalysts on its surface. The most popular method is impregnation [19]. However, other methods such as gas phase deposition [20], ion exchange, and direct addition of the catalytic ion to the gel [21] have also been employed. Cobalt was very frequently loaded into the pores of MCM-41 as the sole ion [22]. Here, we report on the use of nanostructured cobalt oxide inserted in MCM-41 pores using ultrasound radiation. Cobalt carbonyl, $[Co(CO)_3NO]$, was used as the precursor for the synthesis of nanostructured cobalt oxide on MCM-41. The cobalt carbonyl complex was sonicated in the presence of air to yield nanostructured CoO which was deposited on MCM-41. The mesoporous silica (MCM-41) was either prepared by conventional hydrothermal synthesis or sonochemically [23]. The two types of mesoporous silica had the following physical characteristics: hydrothermally prepared MCM-41–surface area 990 m^2/g, pore volume 0.52 cc/g, average pore diameter 2 nm; sonochemically prepared MCM41– surface area 853 m^2/g, pore volume 0.54 cc/g , average pore diameter 2.48 nm.

Nanostructured CoO deposited on either MCM-41 was compared for its activity in the epoxidation of alkenes. Since there was not much of a difference in reactivity using mesoporous silica synthesized by two distinct methods, we decided to use the one prepared by hydrothermal crystallization method for further studies.

Epoxidation of olefins was carried out using CoO-MCM-41 by employing Mukaiyama's method of aerobic oxidation in the presence of a sacrificial reductant such as isobutyraldehyde [24]. Although there are reports of hydrogen peroxide-mediated epoxidation using titanium incorporated on zeolites and MCM-41 [25], the use of molecular oxygen is still important for large-scale industrial preparations. In the present study, the alkene (1 mmole) was treated with isobutyraldehyde (3 equivalents), $NaHCO_3$ (3 equivalents), oxygen (1 atm) and CoO-MCM-41 (2 mole%) at room temperature (28°C) (Table II).

As summarized in Table II, the epoxidation reaction of simple olefins with CoO-MCM-41 catalyst was complete within a few hours (3–6 h). Cyclooctene **1** was epoxidized to cyclooctene oxide **1a** in good yield. Oxidation of *trans*–stilbene **2** yielded *trans*-stilbene epoxide **2a** exclusively, whereas *cis*-stilbene **3** yielded a mixture of *cis* and *trans* epoxides **3a** and **3b** in a ratio of

Table II
Aerobic epoxidation of olefins using CoO-MCM-41 as catalyst

Substate	Time(h)	Product	Yield (%)	Selectivity
 **1**	3	 **1a**	95	
 **2**	3	 **2a**	90	
 **3**	4	 **3a** +  **3b**	92	*trans:cis* 3.6:1
 **4**	5	+diepopxide  **4a**	24 58	
 **5** R = H	3	 **5a**	64	β:α (69:31)
6 R = COCH$_3$	4	**6a**	80	(78:22)
 **7**	3	 **7a**	81	
 **8**	4	 **8a**	75	

3.6 : 1. In the case of citronellol **4**, the corresponding epoxide **4a** was isolated in good yield and there was no oxidation of primary alcoholic functionality.

Epoxidation of cholesterol **5** and its ester proceeded smoothly with moderate diastereoselectivity. Cholesteryl acetate **6** was epoxidized in high yield with preferential formation of 5,6-β-epoxide **6a** (β:$\alpha = 78:22$). In the reaction of cholesterol **5**, the corresponding 5,6-α/β epoxide **5a** was the major product and there was neither the oxidation of secondary alcohol nor isomerization of double bond. Epoxidation of α and β- ionones **7** and **8** yielded good yields of epoxides **7a** and **8a** in which the nonconjugated double bond was epoxidized. The catalyst nanostructured CoO-MCM-41 was centrifuged after the reaction and could be reused successfully without any 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. Under the reaction conditions no epoxide was detected by GC even after several hours.

6. Conclusions

It has been demonstrated that nanostructured amorphous metals, alloys and transition metal oxides prepared using ultrasonication can be used efficiently as catalysts for aerobic oxidation of saturated hydrocarbons under mild conditions. Nanostructured cobalt oxide on MCM-41 catalyzes aerobic epoxidation of alkenes with moderate regio- and stereoselectivity.

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