

## Nanostructured amorphous metals, alloys, and metal oxides as new catalysts for oxidation\*

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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. Nanostructured cobalt oxide on MCM-41 is found to be efficient for catalytic aerobic epoxidation of olefins.

### INTRODUCTION

There is a growing interest in the oxidation of saturated hydrocarbons especially under mild conditions due to its practical and scientific goals. Modern industrial methods usually require high pressure and temperature, while in living organisms the selective functionalization of nonactivated C–H bonds takes place via enzymatic catalysis at room temperature [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], and alkylhydroperoxide [4] are used instead of energy-consuming dioxygen activation. Barton *et al.* have developed a new system that allows the oxidation of saturated hydrocarbons under mild conditions (ambient temperature, atmospheric pressure, and nearly neutral pH). It is known as the Gif system, including iron(II), zinc powder, and oxygen (air), and yields about 20% conversion of initial hydrocarbon in a homogeneous reaction [5]. To overcome the problem of separation of the reaction products a new Gif-KRICT (KRICT stands for Korea Research Institute of Chemical Technology) 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 than that observed by using the Gif system in the homogeneous reaction (5–7%) [7].

Murahashi *et al.* carried out the oxidation of cyclohexane with iron powder and obtained 11% conversion and 70% selectivity for cyclohexanol and cyclohexanone under mild conditions (1 atm O<sub>2</sub>, room temperature, 15 h). The reaction can also be performed without solvent at 70 °C and 8 atm of O<sub>2</sub> with high selectivity [8].

There is no doubt that the use of nanophased catalysts will affect the catalytic activity due to the increase in surface area. However, it was only recently that the superiority of nano-amorphous over nanocrystalline catalysts was demonstrated [9]. Sonochemistry of volatile precursors yield always amorphous nanoproducts.

### STUDIES ON CYCLOALKANE OXIDATION WITH NANOSTRUCTURED 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)<sub>5</sub> and its utility as efficient catalyst in Fischer–Tropsch

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process [9]. They have extended this sonication synthesis to nanophase amorphous cobalt (20 nm) and an amorphous Co/Fe alloy [10]. We were involved in the sonochemical synthesis of amorphous nickel [11] (10 nm) from  $\text{Ni}(\text{CO})_4$  and amorphous Fe/Ni alloy [12] ( $\text{Fe}_{20}\text{Ni}_{80}$ , 25 nm) from a solution of a mixture of  $\text{Fe}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_4$ . The amorphous nature and the particle size were established by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements, respectively [13].

Recently, we reported on the oxidation of cyclohexane up to 40% conversion with 80% selectivity [14] for cyclohexanone and cyclohexanol using nanostructured amorphous metals like Fe and Co and amorphous alloy like  $\text{Fe}_{20}\text{Ni}_{80}$  with oxygen (40 atm) at room temperature (25–28 °C) in the absence of any solvent. In the aerobic oxidation isobutyraldehyde as coreductant and catalytic amount of acetic acid were used. 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 in the absence of amorphous Co, Fe, or alloy as catalysts, no oxidation products were obtained. The oxidation of methylcyclohexane under similar conditions occurs only at the secondary and tertiary C–H bonds, and primary C–H bonds remain unaffected. In the reaction catalyzed by amorphous cobalt the product was found to be a mixture of methyl cyclohexanones and methyl cyclohexanols (1:3) (2-one:3-one:4-one = 28:42:30 and 1-ol:2-ol:3ol:4-ol = 65:9:15:11). When oxidation of cyclohexane was carried out using nanostructured Co (20 nm) catalyst at 70 °C under 40 atm of oxygen for 8 h it was found that the conversion had gone upto 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 °C,  $\text{O}_2$ , 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).

Although we do not have proof for precise mechanism at the present stage, the reaction can be rationalized by assuming the following pathway similar to that suggested by Murahashi [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.

We, however, suspected that due to the high reactivity of the amorphous iron and cobalt nanoparticles it is impossible to avoid their oxidation and in fact the corresponding oxides may be the actual catalysts. To check this hypothesis and to extend the catalytic studies to include iron oxide supported on titania, further work was undertaken.

## STUDIES OF OXIDATION OF CYCLOHEXANE WITH NANOSTRUCTURED AMORPHOUS TRANSITION METAL OXIDES AS CATALYSTS

### Catalyst preparation

All oxide catalysts were prepared by ultrasonic irradiation according to the procedure described earlier [15]. Unlike the argon sonication of the transition-metal (TM) carbonyls which yields the corresponding metals, the sonication under air yields TM oxides. In short, 1 M solution of iron pentacarbonyl or cobalt (III) carbonylnitrosyl in decalin were irradiated under atmospheric pressure at 0 °C for 3 h. The products were washed thoroughly with dry pentane and dried in vacuum. The supported iron oxide/titania catalysts were prepared by the sonication of titanium oxide powder (Degussa P25, surface area 45  $\text{m}^2/\text{g}$ ) with iron pentacarbonyl in decalin under atmospheric pressure at 0 °C for 3 h. To prevent possible decomposition of iron pentacarbonyl, argon was bubbled through a mixture for 1 h before the sonication.

The structure and particle size of the catalysts were established by XRD and TEM. The particle size of the titania-supported catalyst, measured by TEM, was about 40 nm, and it was coated with high-

ly 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 from 0.5 M 4–6 nm.

### Catalytic reactions

When sonochemically prepared iron oxide was used as a catalyst for oxidation of cyclohexane with oxygen (1 atm) and at 70 °C, cyclohexanol and cyclohexanone were obtained (16.5% conversion, 90% selectivity). The ratio of cyclohexanol to cyclohexanone (ol:one) was about 1.5:1. It was observed that part of the highly dispersed iron oxide catalyst (about 25%) went into the solution, during the reaction, forming a deep red color. The rest was found in the powder form. This highly dispersed (8–10 nm) iron oxide catalyst can be considered as a homogeneous–heterogeneous system. Another indication of the importance of the amorphous phase is observed when the crystalline, highly dispersed iron oxide did not form the red color reported above, indicating it was not soluble in the reaction mixture. It means 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 ( $\text{Co}_3\text{O}_4$ ) 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. The results are presented in Table 1. The conversion percentage of the initial product on supported iron oxide/titania catalyst was higher than on unsupported amorphous iron oxide. A control reaction in which titania was used as the catalyst for the oxidation was conducted and demonstrated that titania itself was not effective in the reaction of cyclohexane oxidation. Its functions are therefore the stabilization and activation of iron oxide. The activity of iron oxide–titania catalyst depended also on the conditions of preparation.

### 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, as described elsewhere [17]. Its surface area, measured by the BET nitrogen adsorption method after removal of the surfactant, reached 850 m<sup>2</sup>/g, with a pore size of 1.5 nm and a pore volume of 0.53 ml/g. 0.5 g of titania prepared in this way was put into 80 ml of decalin, and 0.8 ml of iron pentacarbonyl was added to the solution (molar ratio of initial substances was 1:1). The mixture was irradiated by ultrasound under an atmospheric pressure of air at 0 °C for 3 h. The product was washed thoroughly with pentane and dried in vacuum. The surface area of the sample was 570 m<sup>2</sup>/g, with a pore size of 1.3 nm and a pore volume of 0.23 ml/g.

**Table 1** Aerobic oxidation of cyclohexane using highly dispersed transition-metal oxides (1 atm O<sub>2</sub>)

Catalyst	Particle size (nm)	Temp °C	Conversion %	ol:one
Fe <sub>2</sub> O <sub>3</sub>	8–10	70	16.5	1.5:1
Co <sub>3</sub> O <sub>4</sub>	10	70	4.8	1.6:1
Fe <sub>2</sub> O <sub>3</sub> / TiO <sub>2</sub>	30	70	21.3	1.1:1
Fe <sub>2</sub> O <sub>3</sub> / TiO <sub>2</sub> (Mesoporous)		70	26	1.5:1

We have studied the reaction of cyclohexane oxidation with iron oxide supported on mesoporous titania under mild conditions ( $O_2$ , 1 atm; 70 °C). This showed the highest activity in the cyclohexane oxidation. The main products (selectivity almost 90% and conversion 26%) were cyclohexanol and cyclohexanone, in the ratio 1.5:1 (Table 1).

During the reaction, leaching of iron oxide (about 25% of the supported phase) into the solution was observed and the reaction mixture changed its color to deep red. We believe that this happened because of the transfer of oxometal complexes from the support into the liquid phase. After the first reaction cycle, the liquid phase was separated by centrifugation and the experiment was repeated twice, adding fresh portions of cyclohexane and isobutyraldehyde under the same conditions, both with the liquid phase and with the solid phase (previously dried by vacuum). The conversion of the cyclohexane with the liquid phase was only 2.5% (and consisted of about 10% of the conversion with initial iron oxide catalyst supported on mesoporous titania), but with the solid phase the conversion was 17.5% (about 70% of the conversion of cyclohexane in the first reaction cycle). On the basis of these results, it is reasonable to conclude that the sonochemically prepared iron oxide deposited on mesoporous titania is indeed a homogeneous–heterogeneous system fabricating the active oxometal complexes during reaction under oxidation conditions.

### **NANOSTRUCTURED COBALT OXIDE SUPPORTED ON MCM-41: A VERSATILE CATALYST FOR EPOXIDATION OF OLEFINS UNDER AEROBIC CONDITIONS**

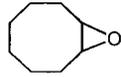
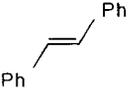
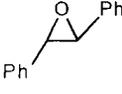
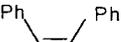
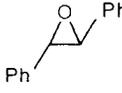
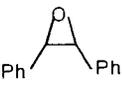
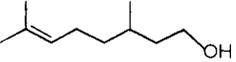
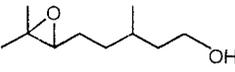
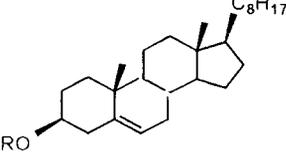
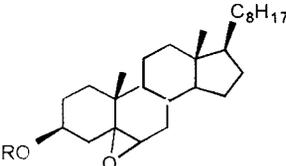
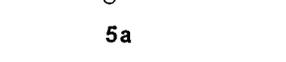
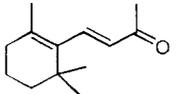
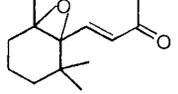
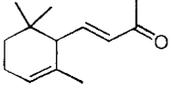
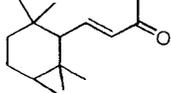
Epoxidation of olefins using molecular oxygen in the presence of transition-metal catalysts has attracted much interest in recent years. Most of the earlier methods of direct epoxidation using molecular oxygen have involved specially designed transition-metal complexes. Search is still ongoing for catalysts that are designer simple 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 stereoselectivity, 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 the 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 as the technique. The 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 MCM-41: 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 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 equiv),  $NaHCO_3$  (3

**Table 2** Aerobic epoxidation of olefins using CoO-MCM-41 as a catalyst.

Substrate	Time(h)	Product	Yield (%)	Selectivity
 <b>1</b>	3	 <b>1a</b>	95	
 <b>2</b>	3	 <b>2a</b>	90	
 <b>3</b>	4	 +  <b>3a</b> + <b>3b</b>	92	trans:cis 3.6:1
 <b>4</b>	5	 <b>4a</b>	58	
 <b>5</b> R = H	3	 <b>5a</b>	64	$\beta$ : $\alpha$ (69:31)
<b>6</b> R = COCH <sub>3</sub>	4	 <b>6a</b>	80	(78:22)
 <b>7</b>	3	 <b>7a</b>	81	
 <b>8</b>	4	 <b>8a</b>	75	

equiv), oxygen (1 atm) and CoO-MCM-41 (2 mole %) at room temperature (28 °C). The results of catalytic epoxidation are summarized in Table 2.

As summarized in Table 2, 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 3.6:1. In 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 epoxidised in high yield with preferential formation of 5,6- $\beta$ -epoxide **6a** ( $\beta$ : $\alpha$  = 78:22). In the reaction of cholesterol **5**, the corresponding 5,6- $\alpha/\beta$  epoxide **5a** was the major product, and there was neither the oxidation of secondary alcohol nor isomerization of double bond. Epoxidation of  $\alpha$ - and  $\beta$ -ionones **7** and **8** yielded good yields of epoxides **7a** and **8a**, in which the non-conjugated 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.

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