

Mesoporous iron–titania catalyst for cyclohexane oxidation

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This is the first report of using ultrasound radiation for depositing a nanosized catalyst (iron oxide) into the pores of a mesoporous material (titania); the resulting catalyst is used for the oxidation of cyclohexane under mild conditions.

The synthesis of mesoporous materials offers a new possibility for the creation of catalysts that are effective in many technological processes. Their high surface area, large adsorption capacity, and ordered pore structure make them very useful for oil refining, petrochemistry, and organic synthesis.¹ At the same time, mesoporous materials have found many applications as supports for metal oxides, organometallic compounds, and other precursors, achieving high dispersion and functionalization of the active phase.² It has been shown that the incorporation of transition metals into the framework of MCM-41 allows the preparation of catalysts which are active in the oxidation of organic compounds.³ The catalytic activity in the liquid-phase oxidation of cyclohexane with aqueous H₂O₂, exhibited by an iron catalyst incorporated into mesoporous molecular sieves (MCM-41), has been attributed to the formation of heterogenized iron complexes.⁴ The yield of target products (cyclohexanol and cyclohexanone) with this catalyst did not exceed 3.5%.

As reported by Suslick *et al.*, the sonochemical method can be used as a tool to prepare nanosized amorphous metals.⁵ If ultrasound irradiation is applied in the presence of an oxide support (such as silica, titania, alumina), the initially formed nanoscale clusters can be trapped in the support. Recently, sonication has been further developed to drive the deposition of iron, nickel, and cobalt on the surface of silica and alumina particles.⁶ Sonochemistry has also been used for the preparation of mesoporous silica (MCM-41),^{7a} mesoporous titania,^{7b} and mesoporous yttria–zirconia. The main advantage in using sonochemistry for the synthesis of mesoporous materials is the drastic shortening of the time involved in the fabrication of the products from days to hours. It has been demonstrated that the wall thickness is perhaps also greater when the sonochemical technique is used. This communication is the first report where sonochemistry is employed to deposit amorphous nanoparticles into the pores of a mesoporous material.

The question as to whether or not sonochemistry can also be used for the deposition of a catalyst into the inner pores of mesoporous materials is examined here. Iron oxide was chosen as a testing probe for this purpose, which can be used as a catalyst in the oxidation of alkanes. We have reported recently on the oxidation of cyclohexane using sonochemically prepared nanostructured amorphous iron and cobalt catalysts or an amorphous iron–nickel alloy.⁸ In that work, the reaction was carried out under high oxygen pressure (40 atm) at room temperature without a solvent, using isobutyraldehyde as an activator and a catalytic amount of acetic acid. Under these conditions, a high conversion of cyclohexane (*ca.* 40%) was obtained with an almost 80% selectivity to the target products cyclohexanone and cyclohexanol. Later it was found that the active catalyst was the nanostructured, sonochemically pre-

pared transition metal (TM) oxide and not the amorphous TM.⁹ In fact, due to the high reactivity of the amorphous materials, it is almost impossible to avoid oxidation of the nanophased TM. We report herein the results of cyclohexane oxidation with an iron oxide catalyst supported over mesoporous titania (MSPT). The preparation of the MSPT and the deposition of the iron oxide into its pores were carried out by a sonochemical method. In our synthesis we have followed the sonochemical preparation of nanophased amorphous Fe₂O₃ described previously.¹⁰ The synthesis was carried out in the presence of mesoporous TiO₂. The activity of this catalyst was tested in the oxidation of cyclohexane under mild conditions.

The mesoporous titanium oxide was synthesized from titanium isopropoxide by ultrasound irradiation, as described elsewhere.^{7b} Its surface area, measured by the BET nitrogen adsorption method (Micromeritics Gemini) after removal of the surfactant, reached 850 m² g⁻¹ with a pore size of 1.5 nm and a pore volume of 0.53 ml g⁻¹.

The as prepared titania was irradiated by ultrasound with a solution of iron pentacarbonyl in decalin under an atmospheric pressure of air at 0 °C for 3 h.¹¹ The surface area of the sample was reduced to 570 m² g⁻¹, with a pore size of 1.3 nm and a pore volume of 0.23 ml g⁻¹. The reduction in surface area and pore volume is due to the insertion of iron oxide into the mesopores.

The particle size of the titanium oxide, obtained from TEM measurements (microscope JEOL-JEM 100) is of the order of 100–200 nm. The outer surface area is *ca.* 1–2 m² g⁻¹ as calculated from the particle size. Coating the outer surface with 5 nm catalyst particles (as estimated from particles found outside the pores) would not lead to the measured reduction in surface area for the titania/iron oxide composite. We, therefore, conclude that the major part of the iron oxide is inserted into the mesopores.

XRD analysis was performed with a Rigaku diffractometer (Model 2028, Cu-K α radiation). In the as prepared sample, iron oxide was in an amorphous state. After heating under argon at 300 °C for 24 h, it crystallized in the form of magnetite.

Elemental analyses, performed using energy dispersive X-ray (EDX) analysis (Link ISIS Oxford) and atomic adsorption spectroscopy (AAS) (Perkin Elmer 2380 spectrometer) showed a difference in iron content (Table 1), the iron concentration obtained by EDX being higher than in the AAS results. This indicates that part of the iron is located on the surface of the catalyst, since EDX measures the surface concentration of the element, while AAS gives the total quantity. Nevertheless, the difference in concentration between these two analytical methods for the catalysts (prepared by the same method of sonochemical irradiation on mesoporous titania support) is lower than on commercial titania (Degussa P-25) (Table 1). This can occur because of the larger pore volume of mesoporous titania in comparison to that of conventional TiO₂ and thus a deeper impregnation of the active phase in the pores.

The binding energy measured by XPS for the Fe2P_{3/2} and Ti 2P_{3/2} did not differ very much for the catalysts supported on

Table 1 Physicochemical properties of iron oxide catalysts prepared by the sonication method

Catalyst	Fe ₂ O ₃ (mass%)		E _b ^a /eV		Conversion of cyclohexane (%)
	EDX	AAS	Fe 2p _{3/2}	Ti 2p _{3/2}	
Fe ₂ O ₃	100	100	710.5 (711.5 ^a)	—	16.5
Fe ₂ O ₃ /TiO ₂ (Degussa P-25)	20.3	12.0	710.6	457.6 (458.6, ^b 459.8 ^c)	21.3
Fe ₂ O ₃ /TiO ₂ (MSPT)	18.7	14.5	710.9	458.7	25.8

^a Value for commercial Fe₂O₃. ^b Value for commercial TiO₂. ^c Value for sonicated TiO₂.

titanium and sonochemically prepared iron oxide and were close to the values corresponding to conventional Fe₂O₃ and TiO₂ (Table 1).

We have studied the reaction of cyclohexane oxidation with iron oxide supported on mesoporous titania under mild conditions.¹² Table 1 presents the conversion of cyclohexane into oxidation products, using three forms of the catalyst: (a) unsupported nanophased amorphous Fe₂O₃; (b) amorphous Fe₂O₃ deposited on TiO₂ (Degussa P-25), which we have reported on previously⁹ and (c) amorphous Fe₂O₃ deposited on TiO₂ (MSPT). Of these the Fe₂O₃/TiO₂ (MSPT) showed the highest activity in cyclohexane oxidation. The main products (selectivity almost 90%) were cyclohexanol and cyclohexanone, in the ratio 1.5:1. GC analysis revealed that in the presence of acetic acid, the activator (isobutyraldehyde) first reacted with oxygen, and the final oxidation product was isobutyric acid. The perisobutyric acid formed *in situ* during this process may react with metal species supported on the carrier to form oxometal complexes. Hydrogen abstraction from cyclohexane by oxometal complexes, followed by the formation of cyclohexanone and cyclohexanol, probably takes place as a result of the same free radical mechanism described earlier.¹³

After the first reaction the liquid phase was separated by centrifugation and the solid catalyst reused under the same conditions.¹² The conversion of a fresh portion of cyclohexane was scarcely changed in comparison with the first cycle. On the basis of these results it is reasonable to conclude that the sonochemically prepared nanosized iron oxide deposited on MSPT is a stable and effective catalyst. It can be used for the oxidation of cyclohexane, other hydrocarbons, and a number of other organic functional groups, which are currently under investigation.

In summary, this work demonstrates that sonochemistry can be used for anchoring nanomaterials in the pores of mesoporous compounds to produce effective catalysts.

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- 11 *Synthesis of mesoporous iron–titania catalyst*: 0.5 g of mesoporous titania prepared by a previously reported method^{7b} was added to 80 ml of decalin, and 0.8 ml of iron pentacarbonyl 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.
- 12 The oxidation of cyclohexane was performed in a thermostated glass reactor using 2 ml (18.5 mmol) of cyclohexane, 2.5 ml (27.75 mmol) of isobutyraldehyde (molar ratio 1.5:1), a catalytic amount of acetic acid (0.06 ml, 1 mmol), and an amount of the catalyst equivalent to 0.015 mmol of iron oxide. The reaction mixture was magnetically stirred at 70 °C and 1 atm of oxygen for 15–17 h. The reaction products were analyzed by GC using the starting alkane as an internal standard. Conversion is defined as the percentage of the starting alkane converted into the products.
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