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Mesoporous iron phosphate as an active, selective and recyclable catalyst for the synthesis of nopol by Prins condensation

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Mesoporous iron phosphate is found to be a highly active and recyclable heterogeneous catalyst for the selective synthesis of nopol by Prins condensation of β-pinene and paraformaldehyde in acetonitrile at 80 °C.

Mesoporous materials having large internal surface areas and narrow pore size distributions have attracted considerable attention ever since the discovery of M41s silica molecular sieves in 1992 due to their wide ranging applications as catalysts, absorbents and host materials.[1] A variety of mesoporous metal oxides,[2–4] aluminosilicates,[5,6] aluminophosphates[7–9] and other transition metal oxide phosphates[10–14] have been developed and synthesized using several supermolecular assembly pathways. Iron phosphate has been reported to be a good catalyst for selective oxidation reactions.[15,16] Mesoporous iron phosphate is expected to have interesting and novel catalytic properties. Yan *et al.* have reported the synthesis of mesoporous iron phosphate using a fluoride route.[17]

Terpenes are highly useful materials in the synthesis of a variety of products such as food additives, pharmaceuticals, agrochemicals and aromas. Nopol is an optically active bicyclic primary alcohol used in the agrochemical industry to produce pesticides and also in the manufacture of soaps, detergents, polishes and other household products.[18] The general method of its production is by Prins condensation of β-pinene and *para*-formaldehyde using (i) zinc chloride as catalyst at 115–120 °C for several hours (57% yield of nopol), (ii) acetic acid as catalyst at 120 °C which yields nopyl acetate which is then saponified to nopol and (iii) autoclaving a mixture of β-pinene and *para*-formaldehyde at 150–230 °C for several hours yielding quantitative amounts of nopol.[19] All the above methods form monocyclic isomers and other side products. Recently Montes de Correa *et al.* have reported the synthesis of nopol over Sn-MCM-41 molecular sieves in the presence of toluene as a solvent at 90 °C.[20] However, Sn is not often a desirable constituent due to its toxic nature.

There has been an increasing interest in recent years in developing environmentally benign and clean technologies, products and processes with economic benefits. The replacement of harmful volatile organic solvents with less harmful alternative reaction media and achieving high atom economy are some of the clean synthetic methodologies. There is also a great demand to develop highly selective heterogeneous catalyst based technologies under mild reaction conditions without employing toxic materials. Herein we report the selective synthesis of nopol over a mesoporous iron phosphate catalyst in the presence of a relatively benign solvent, acetonitrile, under relatively mild reaction conditions.

Mesoporous iron phosphate was synthesized by a procedure similar to that described by Yan *et al.*[17] A typical synthesis procedure involves the precipitation of $FePO_4$ from an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ (20 mmol) and Na_2HPO_4 (50 mmol). The precipitated $FePO_4$ was separated by centrifugation and washed several times with distilled water. The precipitate was then suspended in an acidified (HF) solution followed by the addition of ~ 1 M solution of sodium dodecyl sulfate (10 mmol) at room temperature with stirring for 30 minutes. The resultant mixture was heated to 60 °C and kept for 2.5 h. The mixture was then cooled to room temperature, centrifuged, washed with water and acetone when a light yellow solid was obtained which was dried at room temperature. The surfactant was removed from the catalyst by mixing it with 0.05 M sodium acetate in ethanol and stirring at room temperature for 40 minutes. It was then separated by centrifugation, washed several times with ethanol and dried at room temperature. The removal of surfactant was confirmed by an FT IR analysis of the sample before and after the surfactant removal step.

The synthesized catalyst was characterized by X-ray diffraction analysis using a Siemens D5000 diffractometer with a Cu-Kα radiation running at 40 KV/30 mA in the 2θ range 1° to 70° with a step size of 0.05°. Single point BET surface area of the catalyst was determined using N_2 adsorption at −196 °C (77 K) using a Micromeritics Autochem. II Instrument (Model 2920). A nitrogen sorption experiment was also carried out using the same instrument at −196 °C under different N_2/He pressure ratios to determine the type of adsorption.

An X-ray diffractogram of synthesized iron phosphate shows diffraction peaks at 2θ of 2.3–2.4° and no peaks at higher diffraction angles (Fig. 1). The low-angle diffraction peaks confirm the mesoporous structure of the synthesized iron phosphate sample. The synthesized $FePO_4$ shows a specific surface area of 272 $m^2\ g^{-1}$. The nitrogen adsorption/desorption pattern shows a type IV isotherm, again typical of mesoporous materials.

Table 1 shows the results of nopol synthesis† by the Prins condensation of β-pinene and paraformaldehyde over mesoporous $FePO_4$ catalyst. Different experimental parameters such as the effect of solvent, catalyst amount, reaction temperature and reaction time were studied. It was found that quantitative yields of nopol could be synthesized using mesoporous iron phosphate catalyst in the presence of acetonitrile solvent at 80 °C (entry 17). Control experiments showed no reaction in the absence of the catalyst (entry 10). Acetonitrile was found to be the most suitable solvent (entry 1) followed by toluene (entry 2), dichloromethane (entry 3), dioxane (entry 4), and cyclohexane (entry 5). No appreciable reaction was observed in methanol solvent (entry 6). Maximum conversion was observed at 80 °C. A β-pinene–paraformaldehyde ratio of 1 : 2 is generally used for the reaction. However, a 1 : 1 ratio was also found to be equally good (entry 9). A comparison of the activity of the mesoporous material with that obtained by a conventional precipitation technique showed a lower activity for the latter (entry 16).

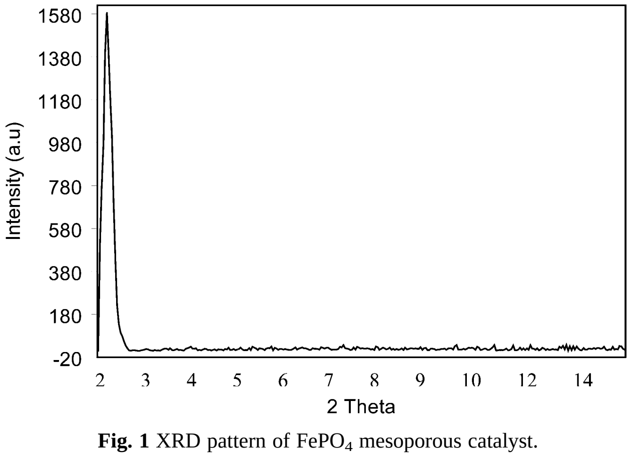

Fig. 1 XRD pattern of $FePO_4$ mesoporous catalyst.

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The heterogeneous $FePO_4$ catalyst was separated from the reaction mixture by first washing the reaction mixture with acetone followed by hot water to remove the organics and unreacted paraformaldehyde. The recovered $FePO_4$ catalyst was washed many times with acetone and dried at 110 °C overnight and reused several times without any loss of activity or product selectivity (Table 2).

The formation of nopol from β-pinene and formaldehyde occurs through an addition reaction between the two reactants in the presence of an acid catalyst. It has been known that weak and medium acid sites are responsible for Prins condensation reactions.[21] A comparison of the temperature programmed desorption of ammonia (TPD) studies on the the synthesized $FePO_4$, a magnesia (a basic material) sample and an alumina (weakly acidic material) sample showed a total ammonia heat of adsorption of -24.4 kJ mol^{-1} for $FePO_4$, -15.8 kJ mol^{-1} for MgO and -25.8 kJ mol^{-1} for alumina, thereby suggesting that $FePO_4$ possesses weakly acidic properties which may be responsible for its activity.

Table 1 Nopol synthesis by Prins condensation of β-pinene and paraformaldehyde over $FePO_4$

Entry	Catalyst amount (g)	Solvent	Solvent amount (mL)	Temperature (°C)	Reaction time (h)	Nopol yield (%)
1	0.10	Acetonitrile	10	80	6	51
2	0.10	Toluene	10	80	6	35
3	0.10	Dichloromethane	10	80	6	26
4	0.10	Dioxane	10	80	6	24
5	0.10	Cyclohexane	10	80	6	20
6	0.10	Methanol	10	80	6	02
7	0.10	Acetonitrile	5	80	6	43
8	0.10	Acetonitrile	20	80	6	30
9	0.10[a]	Acetonitrile	10	80	6	48
10	0.00	Acetonitrile	10	80	6	00
11	0.01	Acetonitrile	10	80	6	08
12	0.025	Acetonitrile	10	80	6	22
13	0.05	Acetonitrile	10	80	6	29
14	0.20	Acetonitrile	10	80	6	55
15	0.50	Acetonitrile	10	80	6	82
16	0.50[b]	Acetonitrile	10	80	6	58
17	1.00[c]	Acetonitrile	10	80	6	100
18	0.10	Acetonitrile	10	30	6	07
19	0.10	Acetonitrile	10	50	6	30
20	0.10	Acetonitrile	10	70	6	45
21	0.10	Acetonitrile	10	80	4	22
22	0.10	Acetonitrile	10	80	4	22
23	0.10	Acetonitrile	10	80	8	57
24	0.10	Acetonitrile	10	80	12	62
25	0.10	Acetonitrile	10	80	24	85

Reaction conditions: 5 mmol β-pinene, 10 mmol paraformaldehyde.[a] 5 mmol β-pinene, 5 mmol paraformaldehyde. [b] $FePO_4$ obtained by conventional precipitation. [c] Reaction time = 4 h.

Table 2 Recyclability of $FePO_4$ catalyst for the Prins condensation of β-pinene and paraformaldehyde to nopol in acetonitrile at 80 °C

Reaction cycle	Conversion (%)	Nopol selectivity (%)
1	82	100
2	83	100
3	82	100
4	81	100
5	81	100

Reaction conditions: 5 mmol β-pinene, 10 mmol paraformaldehyde, 10 mL acetonitrile, 0.5 g $FePO_4$, 80 °C, 6 h.

In summary, the present study shows that mesoporous $FePO_4$ is a novel and active catalyst for the selective synthesis of nopol by Prins condensation of β-pinene and paraformaldehyde in the presence of a relatively benign solvent, acetonitrile, under relatively milder reaction conditions. The catalyst does not contain any toxic constituents, emphasizing its environmentally benign nature. The catalyst is also easily separable from the reaction mixture and reusable without any loss of activity and selectivity up to five cycles. This protocol also does not employ any chlorinated or hydrocarbon based organic solvents.

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Notes and references

† Synthesis of nopol was conducted in liquid phase in a 100 mL round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. In a typical reaction procedure, 5 mmol of β-pinene was mixed with 10 mmol of paraformaldehyde and 0.10 g catalyst in 10 mL solvent in the R.B. The mixture was then vigorously stirred at atmospheric pressure for the desired time period at 80 °C. After the reaction, the mixture was extracted with acetone and analyzed by a Hewlett-Packard 6890 Gas Chromatograph using an HP-Innowax polyethylene glycol capillary column (30 m × 320 μm × 0.25 μm) and a quadrupole mass filter equipped HP 5973 mass selective detector. Identification of the product was done using the GC-MS as well as by comparing the retention time of the standard. Quantification of the products was obtained using a multi-point calibration curve.

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