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Silica supported-double metal cyanides (DMCs): A green and highly efficient catalytic protocol for isomerisation of 2′-hydroxychalcones to flavanones

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ABSTRACT

Four different double metal cyanides (NiHCFe, CrHCFe, MnHCFe and ZnHCFe) were synthesized, followed by adsorbed on silica gel and used as Lewis acid catalyst in the isomerisation of substituted 2′-hydroxychalcones to flavanones under solvent-free (dry) condition. Optimization of the reaction condition, temperature effects, DMC catalysts loading and re-useable catalytic activity were further studied during the reaction. Among these catalysts, NiHCFe at 35 mol% loading gave excellent yield (90%) at 100 °C temperature in 1.15 h. Catalyst (NiHCFe) easily recovered and re-used six times without much loss of its catalytic activity which gave 80–85% product yields each time. However, these DMCs were failed to give product in the solution phase even prolonging the reaction time at reflux temperature. Similarly, isomerization of substituted 2′-aminochalcones gave 2–5% yields either in solution phase or under solvent-free condition.

1. Introduction

Flavanones (2,3-dihydroflavones) are central intermediate in the biogenesis of flavonoids and are present in plants as the largest single group conferring oxygen ring compounds [1]. They have no direct involvement in the growth and development of plants. However, they play an important role in protecting the plants from microbes and insects attack [2]. These polyphenolic molecules are the most fascinating and useful secondary metabolites which constitute an important component of human diet and known for their antioxidant activities [3,4]. They have further diverse spectrum of biological activities that include hepatoprotectors, hypotensive, antifungal, antibacterial and antitumor [5–8]. In the synthesis of pharmaceutical and biological significance molecules, they are widely used as synthons in the laboratory [9].

In the biogenesis, 2′-hydroxychalcones gave flavanones in the presence of enzyme chalcone isomerase [10]. Therefore, 2′-hydroxychalcones are commonly used in the flavanones synthesis under different acid and base [11,12] catalysts, thermolysis, electrolysis and photolysis [13] in the laboratories. These reactions gave variable yields (20–90%) depending upon the substituents on the aromatic rings. Flavanones have also been prepared using other methods like condensation of phenylpropiolic acid with phenols [14,15]; solvent free synthesis using MW-irradiation of phloroglucinol and β-ketoesters [16]; using phase transfer catalysts like tetrabutylammonium iodide, tetrabutylphosphonium bromide, hexadecyltrimethylammonium bromide; organocatalysts like glycine, L-proline, L-alanine, L-leucine and pyridine; ZnO supported-metal oxide (MgO, BaO, K_2O and Na_2O) catalysts under solvent free condition at high temperature [17–20] and MgO- and ZnO-impregnated with various other supports as HZSM-5, Al_2O_3 and SiO_2 [21–24]. Generally, it was observed that the yield of flavanone is less in solid-supported catalysts up to 100 °C might be due to less adsorption on the active sites and at high temperature (above 160 °C), the yield of flavanone is reduced due to prevention of adsorption [25]. To obviate such problems, recently several activators/promoters such as Lewis acids and metal salts, MW, ultrasound and solid support methods have been introduced [26–28]. However, some of these procedures have drawbacks such as long reaction time, decomposition, low yields, use of toxic reagents and tedious work up procedures [29–31] due to high temperature and deactivated and sterically hindered aromatic rings. Therefore, we have interest in new catalytic system for the synthesis of flavanones. Indeed, we need to develop an efficient and green protocol due to the growing awareness about environmental concerns. Therefore, the organic chemists are under increasing pressure to alter current working practices for the sustainable development in academia and industry research and to find environmentally benign and greener alternatives.

The solid support chemistry has been used for many syntheses [32]. Among the various advantages that solid-phase synthesis offers are the ability to use excess quantities of reagents to force reactions to completion and the easy of product isolation by simple filtration, thus affording the clean products with no further

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need for conventional work-up and purification. Therefore, homogeneous catalysts have been extensively investigated, but only few heterogeneous catalysts have been found. Heterogeneous catalysts in the organic synthesis have special interest from environmental and economical point of view. They have high turn-over numbers and easily separated from reaction mixtures. Similarly, it is found that the cyclization reaction of hydroxy group to a carbon–carbon unsaturated bond (like 2′-hydroxychalcones) is thermodynamically feasible but has high activation barriers.

The double metal cyanides (DMCs) are heterogeneous catalysts which have zeolite-type case structure and contain only Lewis acid sites [33]. These lowers the activation energy and so used as industrially applied solid Lewis catalysts for the ring opening and polymerization of epoxides producing polyether–polyols [34], transesterification of carbonates [35] and multi-component coupling reactions [36]. They were also reported as catalysts in hydroamination, copolymerization of CO_2 with propylene, cyclohexene and other epoxide ring opening reactions [37–39].

We report herein first time the use of NiHCFe, CrHCFe, MnHCFe, ZnHCFe catalysts for the isomerisation of 2′-hydroxychalcone to flavanone using silica gel support under solvent-free condition.

2. Experimental

2.1. Reagents and materials

The reagents (chemicals) were purchased from commercial sources and used without further purification. All reactions were monitored by TLC using pre-coated silica gel aluminum plates (contain ~13% $CaSO_4$ ½ H_2O, silica gel/UV_{254}) purchased from Merck. Visualization of TLC plates was accomplished with UV lamp (short UV, 254 nm) and charring with 5% methanolic H_2SO_4 spray reagent. Metal hexacyanoferrate (MHCFe) was synthesized from potassium hexacyanoferrate (II), following Alam et al. method [40–42]. Chalcone derivatives were synthesized according a reported procedure [43,44].

2.2. Equipment

Melting points were recorded on perfit apparatus and are uncorrected. Elemental analysis was performed on a Vario EL–HNS analyzer. FT infrared (FTIR) spectra were recorded on a Nexus Thermo Nicolet FT-IR spectrometer using KBr pellets. ^1H and ^{13}C NMR spectra were recorded in deuterated chloroform ($CDCl_3$) on a 500 MHz and 125 MHz (Bruker) respectively. Chemical shifts are given in parts per million (ppm) referenced to TMS.

2.3. Preparation of metal hexacyanoferrates (II)

A solution of potassium hexacyanoferrate (II) (167 mL, 0.1 M) was slowly added to an aqueous solution of the respective metal nitrate (500 mL, 0.1 M) with constant stirring at room temperature. A slight excess of metal salt was used for complete precipitation. A reaction mixture was then heated at 60 °C on a water bath for 2–3 h and kept as such for 24 h at ambient temperature. After 24 h, the precipitate was filtered on a Buckner funnel, washed thoroughly with Millipore water and dried in an oven at 60 °C. The dried product was powdered and sieved with 100 mesh size.

2.4. General procedure for the adsorption of double metal cyanide on silica

To a mixture of double metal cyanide (DMC, 35 mol%, CrHCFe – 12.5 mg; MnHCFe – 11.6 mg; NiHCFe – 12 mg; ZnHCFe – 13.3 mg) and silica gel (3 mmol, 180.24 mg) was added minimum amount of water. The slurry was stirred and grinded for 2 min, followed by completely dried by heating under vacuum. DMCs-silica gel adsorbed catalysts were directly used in the reaction.

2.5. General procedure for the synthesis of flavanones

2′-Hydroxychalcone (1 mmol) in minimum $CHCl_3$ was added drop wise on a mixture of silica gel (3 mmol, 180.24 mg) and NiHCFe catalyst (35 mol%, 12 mg) or 2′-hydroxychalcone (1 mmol) in minimum $CHCl_3$ was added drop wise on DMCs–silica gel adsorbed catalysts (190–192 mg). Followed by evaporation of solvent, the reaction mixture was stirred and grinded at 100 °C temperature. Thin layer chromatography (TLC) monitoring, the reaction was completed in 1–1.15 h. The reaction mixture was cooled, dissolved in dichloromethane (CH_2Cl_2) and filtered DMC catalyst dried under vacuum for re-use. Dichloromethane solvent was evaporated in vacuo and recrystallized from methanol to obtain the pure product.

2.6. Characterization data for compounds ***1b–20b***

2-(4-Methoxyphenyl)-2,3-dihydrochromen-4-one (**1b**): Yield 80%; light yellow solid; mp: 95–96 °C (Lit. [45] 95–97 °C); IR ν_{max} (KBr, cm^{-1}): 2956, 2923, 1680 (C=O), 1590, 1320, 1225; ^1H NMR (500 MHz, $CDCl_3$): δ 7.81 (dd, 1 H, J = 8.0 and 2 Hz), 7.52–7.48 (m, 1H), 7.41 (d, 2H, 8.5 Hz), 7.07–7.03 (m, 2H), 6.96 (dd, 2H, J = 8.5 and 1.5 Hz), 5.43 (dd, 1H, J = 13.5 and 2.5 Hz), 3.85 (s, 3H), 3.11 (dd, 1H, J = 16.5 and 13.5), 2.86 (dd, 1H, J = 17.0 and 3 Hz).

2-(4-Bromophenyl)-2,3-dihydrochromen-4-one (**2b**): Yield 90%; light yellow solid; mp: 119 °C (Lit. [46] 118–119 °C); IR ν_{max} (KBr, cm^{-1}): 2965, 2930, 1685 (C=O), 1566, 1300, 1230; ^1H NMR (500 MHz, $CDCl_3$): δ 7.82 (dd, 1H, J = 8.0 and 2 Hz), 7.48–7.59 (m, 3H), 7.34–7.49 (m, 2H), 7.03–7.10 (m, 2H), 5.47 (dd, 1H, J = 13.0 and 3 Hz), 3.04 (dd, 1H, J = 16 and 13.0 Hz), 2.88 (dd, 1H, J = 16 and 3 Hz).

2-(3,4-Dimethoxyphenyl)-2,3-dihydrochromen-4-one (**3b**): Yield 78%; light yellow solid; mp: 148–149 °C; IR ν_{max} (KBr, cm^{-1}): 2954, 2934, 1676 (C=O), 1545, 1322, 1221; ^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (dd, 1H, J = 1.5 Hz, J = 7.8 Hz), 7.53 (d, 1H, J = 7.5 Hz), 7.51 (dd, 1H, J = 8 and 2 Hz),7.40 (dd, 1H, J = 8 and 6 Hz), 7.36 (d, 1H, J = 2 Hz), 6.96 (d, 1H, J = 8 Hz), 6.72 (s, 1H), 5.43 (dd, 1H, J = 13.5 and 2.5 Hz), 3.98 (s, 3H), 3.95 (s, 3H), 3.11 (dd, 1H, J = 16.5 and 13.5 Hz), 2.86 (dd, 1H, J = 17.0 and 3 Hz). ^{13}CNMR (125 MHz, $CDCl_3$) 178.3, 163.3, 156.1, 152.1, 149.3, 133.6, 125.6, 124.2, 123.9, 120.0, 118.0, 111.2, 108.8, 106.4, 56.1.

2-(3,4,5-Trimethoxyphenyl)-2,3-dihydrochromen-4-one (**4b**): Yield 75%; light yellow solid; mp = 165–166 °C; IR ν_{max} (KBr, cm^{-1}): 2956, 2923, 1680 (C=O), 1630, 1600, 1590, 1320, 1300, 1225, 964; ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, 2H, J = 8 Hz), 6.95 (d, 2H, J = 8 Hz), 6.66 (d, 1H, J = 2.5 Hz), 6.78 (d, 1H, J = 2.5 Hz), 5.32 (dd, 1H, J = 13.5 and 2 Hz), 3.88 (s, 9H), 2.70 (dd, 1H, J = 13.5 and 2.0 Hz), 2.98 (dd, 1H, J = 16.8 and 13.0 Hz).

2-(3-Nitrophenyl)-2,3-dihydrochromen-4-one (**5b**): Yield 89%; light yellow solid; mp = 173–174 °C (Lit. [47] 174–176 °C); IR ν_{max} (KBr, cm^{-1}): 2956, 2923, 1698 (C=O), 1630, 1527 (CH = CH), 1490 (CNO_2), 1320, 1230, 965. ^1H NMR (500 MHz, $CDCl_3$); 8.2 (s, 1H), 8.12 (dd, 2H, J = 14 and 3 Hz), 7.6 (d, 1H, 16 Hz), 7.52 (d, 2H, 14 Hz), 6.95 (d, 2H, J = 8 Hz), 5.8 (dd, 1H, J = 13.5 and 2 Hz), 3.11 (dd, 1H, J = 16.5 and 13.5 Hz), 2.86 (dd, 1H, J = 17.0 and 3 Hz).

7-Methoxy-2-(3-nitrophenyl)-2,3-dihydrochromen-4-one (**6b**): Yield = 86%. light yellow solid; mp = 89 °C; IR ν_{max} (KBr, cm^{-1}): 2985, 1627 (C=O), 1630, 1527, 1486 (CNO_2), 1320, 1224. ^1H NMR (500 MHz, $CDCl_3$); 8.2 (s, 1H), 8.12 (dd, 1H, J = 13 Hz), 7.6 (d, 1H, 16 Hz), 7.52 (d, 2H, 14 Hz), 6.95 (d, 2H, J = 8 Hz), 5.8 (dd, 1H, J = 13.5 and 2 Hz), 3.73 (s, 3H), 3.11 (dd, 1H, J = 16.5 and 13.5 Hz), 2.86 (dd, 1H, J = 17.0 and 3 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 196.9, 165.7, 157.9, 148.6, 141.6, 133.3, 130.4, 129.9, 122.4, 120, 112.7, 105.8, 100.4, 78, 55.9, 42.8.

2-(4-Chlorophenyl)-7-methoxy-2,3-dihydrochromen-4-one (**7b**): Yield = 85%; light yellow solid; mp = 122 °C (Lit. [48] 120–121 °C); IR ν_{max} (KBr, cm^{-1}): 2972, 2910, 1688 (C = O), 1553, 1315, 1223; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.81 (dd, 1H, J = 8.0 and 2 Hz), 7.47–7.57 (m, 3H), 7.34–7.49 (m, 2H), 7.03–7.10 (m, 2H), 5.45 (dd, 1H, J = 13.0 and 2.5 Hz), 3.73 (s, 3H), 3.04 (dd, 1H, J = 16 and 13.0 Hz), 2.86 (dd, 1H, J = 16 and 3 Hz).

2-(4-Chlorophenyl)-5,7-dimethoxy-2,3-dihydrochromen-4-one (**8b**): Yield = 86%; light yellow solid. mp = 101 °C; IR ν_{max} (KBr, cm^{-1}): 1687 (C=O); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.82 (dd, 2H, J = 8.0 and 2 Hz), 7.13 (dd, 2H, J = 8.0 and 2 Hz), 5.95 (s, 1H), 5.91 (s, 1H), 5.51 (dd, 1H, J = 13.5 and 2.5 Hz), 3.73 (s, 6H), 3.13–3.38 (dd, 1H, J = 17 and 13.5 Hz), 2.86 (dd, 1H, J = 17 and 2.5 Hz). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 196.9, 166.7, 161.7, 158.9, 138.8, 133.2, 129.1, 128.6, 101, 92.7, 91.9, 79, 55.9, 43.1.

2-p-Tolyl-2,3-dihydrochromen-4-one (**9b**): Yield = 80%; light yellow solid; mp = 70–71 °C (Lit. [41] 68–70 °C); IR ν_{max} (KBr, cm^{-1}): 2985, 1627 (C=O), 1630, 1527, 1320, 1224. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.84 (dd, 1H, J = 8 and 2 Hz), 7.53–7.47 (m, 1H), 7.43–7.41 (m, 2H), 7.39–7.31 (m, 2H), 7.02–6.93 (m, 2H), 5.37 (dd, 1H, J = 13.0 and 2.5 Hz), 3.00 (dd, 1H, J = 14.5 and 13.0 Hz), 2.787 (dd, 1H, J = 17 and 3 Hz), 2.30 (s, 3H).

7-Methoxy-2-p-tolyl-2,3-dihydrochromen-4-one (**10b**): Yield = 81%; light yellow solid; mp = 67 °C; IR ν_{max} (KBr, cm^{-1}): 2985, 1679 (C=O), 1630, 1527, 1320, 1224. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.84 (dd, 1H, J = 8 and 2 Hz), 7.53–7.47 (m, 1H), 7.43–7.41 (m, 2H), 7.39–7.31 (m, 2H), 7.02–6.93 (m, 2H), 5.37 (dd, 1H, J = 13.0 and 2.5 Hz), 3.46 (s, 3H), 3.00 (dd, 1H, J = 14.5 and 13.0 Hz), 2.787 (1H, dd, J = 17 and 3 Hz), 2.30 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 198, 165, 159, 139, 138.3, 132.1, 129.8, 127.4, 112.3, 105.8, 100.4, 79.3, 58.1, 46.2, 24.7.

5,7-Dimethoxy-2-p-tolyl-2,3-dihydrochromen-4-one (**11b**): Yield = 83%; light yellow solid; mp = 72 °C; IR ν_{max} (KBr, cm^{-1}): 1694 (C=O). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.90 (d, 2H, J = 8.4 Hz), 6.95 (d, 2H, J = 8.8 Hz), 6.66 (d, 1H, J = 2.5 Hz), 6.78 (d, 1H, J = 2.5 Hz), 5.32 (dd, 1H, J = 13.5 and 2.0 Hz), 3.88 (s, 6H), 2.70 (dd, 1H, J = 13.5 and 2.0 Hz), 2.98 (dd, 1H, J = 16.8, 13.0 Hz), 2.26 (s, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 196.9, 166.7, 161.7, 158.9, 137.7, 137.3, 129.3, 127.1, 101, 92.7, 91.9, 79, 55.9, 52.7, 43.1, 24.3.

2-(4-Hydroxy-3-methoxyphenyl)-2,3-dihydrochromen-4-one (**12b**): Yield = 60%; light yellow solid; mp = 96 °C; IR ν_{max} (KBr, cm^{-1}): 1672 (C=O). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.0 (s, br, OH, 1H), 7.45 (m, 2H), 7.10 (m, 2H), 6.85 (m, 1H), 6.58 (m, 1H), 6.53 (m, 1H), 5.51 (dd, 1H, J = 13.5 and 2.0 Hz), 3.73 (s, 3H), 3.13–3.38 (dd, 1H, J = 14.5 and 13.0 Hz), 2.78 (dd, 1H, J = 17 and 3 Hz). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 199.1, 157.1, 153.1, 145.6, 135.2, 131.9, 129.6, 122.1, 121.6, 120.0, 118.9, 115.2, 112.6, 76.1, 55.1, 43.9.

2-(3-Nitrophenyl)-2,3-dihydrochromen-4-one (**13b**): Yield = 70%; light yellow colour solid; mp = 70 °C; IR ν_{max} (KBr, cm^{-1}): 1683 (C=O). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.15 (s, 1H), 8.13 (d, 1H, J = 16 Hz), 7.79 (d, 1H, J = 12 Hz), 7.58 (d, 1H, J = 13 Hz), 7.45 (dd, 1H, J = 13 and 3 Hz), 7.32–7.30 (m, 1H), 6.91–6.88 (m, 2H), 5.51 (dd, 1H), 3.13–3.38 (dd, 1H, J = 17 and 13.5 Hz), 2.86 (dd, 1H, J = 17 and 2.5 Hz).

2-(4-Chlorophenyl)-2,3-dihydrochromen-4-one (**14b**): Yield = 90%; light yellow colour solid; mp = 83 °C (Lit. [45] 84–85 °C); IR ν_{max} (KBr, cm^{-1}): 2985, 1627 (C=O), 1630, 1320, 1224. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.86 (d, 1H, J = 8 Hz), 7.50–7.55 (m, 1H), 7.40–7.46 (m, 4H), 7.05–7.11 (m, 2H), 5.47 (dd, 1H, J = 13.0 and 3 Hz), 3.07 (dd, 1H, J = 17 and 13.0 Hz), 2.87 (dd, 1H, J = 17 and 3 Hz).

2-Phenyl-2,3-dihydrochromen-4-one (**15b**): Yield = 80%; light yellow solid; mp = 76 °C (Lit. [45] 78–79 °C); IR ν_{max} (KBr, cm^{-1}): 2990, 1664 (C=O), 1630, 1320, 1242. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.86 (d, 2H, J = 8 Hz), 7.45–7.36 (m, 3H), 7.60 (dd, 1H, J = 8.4 and 3.0 Hz), 7.20–7.0 (m, 2H), 6.91 (m, 1H), 5.3 (dd, 1H, J = 14 and 3 Hz), 2.73 (dd, 1H, J = 14.0 and 3 Hz), 2.97 (dd, 1H, J = 17.0 and 14.0 Hz).

2-(4-Dimethylaminophenyl) chroman-4-one (**16b**): Yield 30%; light yellow solid; mp: 119–120 °C (Lit. [46] 116–117 °C); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.85 (dd, 1H, J = 8.3 and 1.7 Hz), 7.46–7.52 (m, 1H), 7.35 (d, 2H, J = 8.7 Hz), 7.00–7.05 (m, 2H), 6.77 (d, 2H, J = 8 Hz), 5.38 (dd, 1H, J = 13.3 and 2.8 Hz), 3.16 (dd, 1H, J = 17 and 14 Hz), 2.98 (s, 6H), 2.87 (dd, 1H, J = 17 and 3 Hz).

2-(4-Bromophenyl)-2,3-dihydroquinolin-4(1H)-one (**17b**): Yield 3%; yellow colour solid; mp = 161 °C (Lit. [49] 160 °C).

2-(4-Methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (**18b**): Yield 5%; yellow colour solid; mp = 145 °C (Lit. [49] 145 °C).

7-Bromo-2-(4-nitrophenyl)-2,3-dihydroquinolin-4(1H)-one (**19b**): Yield 3%; yellow colour solid; mp: > 250 °C (Lit. [29] >250 °C).

2-(3,4-Dimethoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (**20b**): Yield 2%; yellow semi solid (Lit. [49] semisolid).

3. Results and discussion

3.1. Characterization of (DMCs)

3.1.1. CHN, TGA/DTA, XRD

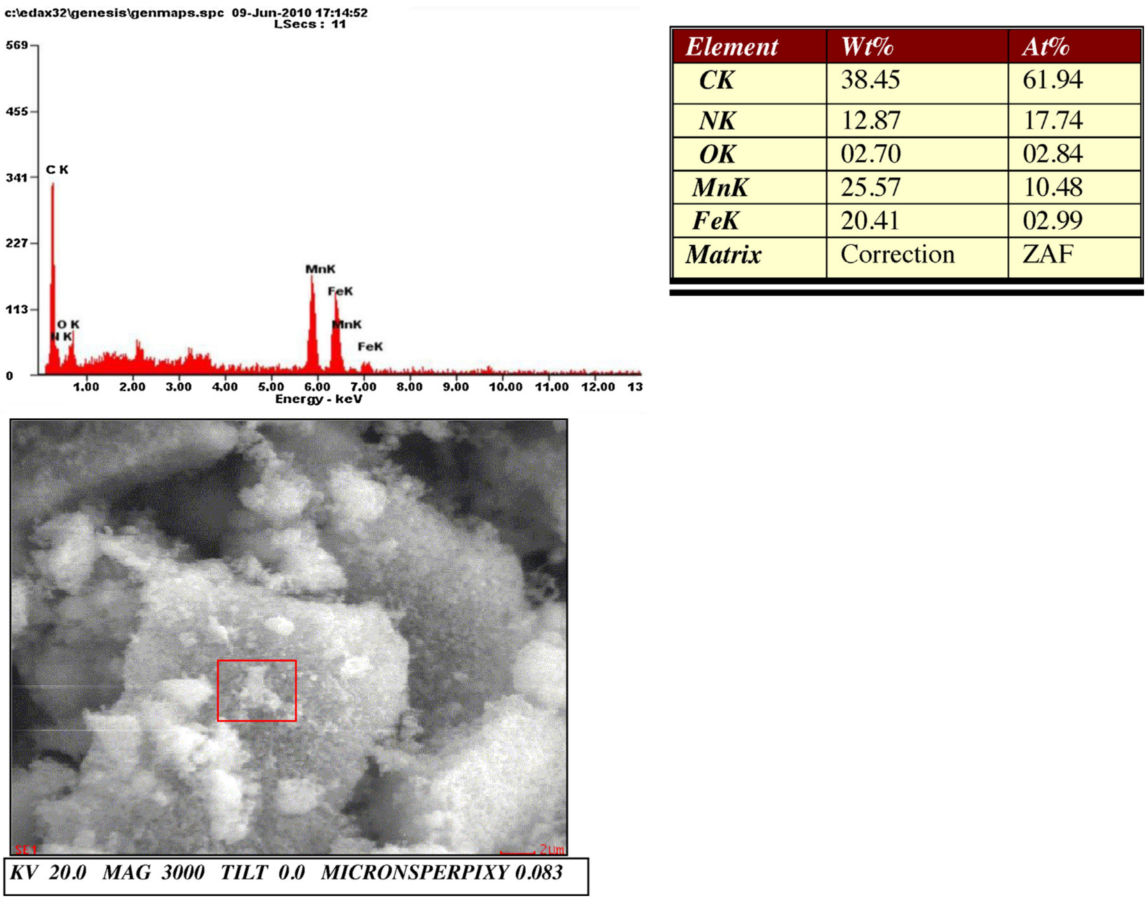
The percentage of carbon, hydrogen and nitrogen present in MHCFe (II) were recorded on an Elementar Vario ELHI CHNS analyzer. In order to measure the water of crystallization present in MHCFe, thermo gravimetric analysis (TG) was carried out with the thermal analyzer (EXSTAR TG/DTA 6300, SII Nano Technology Inc., Japan). The heating rate was 10 °C/min. All measurements were carried out in a static air atmosphere using Al_2O_3 as a reference. The purity of MHCFe was checked by comparing the X-ray diffraction (Brucker AXS D8 Advance) data of the complex. The relative-intensity data and inter planner spacing (d) were in good agreement with the reported values.

3.1.2. Surface area measurement

The Brunauer–Emmett–Teller (BET) method has been used to determine the surface area of MHCFe complexes on a surface area analyzer (micromeritics ASAP 2010, UK). In this technique, the surface area was determined by physical adsorption of gases at their boiling temperatures. The determined values of the surface areas are: 25.91, 2.55, 68.07 and 158.30 m^2 g^{-1} in case of Cr-, Mn-, Ni-, Zn-HCFe(II), respectively.

The MnHCFe surface area (2.55 m^2 g^{-1}) is low. It might be due to higher magnetic behaviour of manganese (agglomeration occurs) compared to that of other metal present in MnHCFe. It was further verified by FE-SEM (Field Emission Scanning Electron Microscopy). FE-SEM images were recorded using a FEI Quanta 200F microscope operating at 20 kV. The microscope was also used to record the EDXA (Energy dispersive X-ray analysis) spectra. Elements present in the MnHCFe were verified by the EDXA spectrum too. SEM images showed the shape and surface morphology of the MnHCFe (Fig. 1).

The XRD pattern of CrHCFe, MnHCFe, NiHCFe and ZnHCFe were analyzed using JCPDS (Joint Committee on Powder Diffraction Standards) diffraction files. The JCPDS data of MHCFe were carefully compared. All the diffraction peaks of the experimental pattern matched with those of the relative intensities of the compounds MnHCFe (JCPDS file number 48–0910) (Fig. 2), NiHCFe (JCPDS file number 14–0291) (Fig. 3) and ZnHCFe (JCPDS file number 01–0433) (Fig. 4). Chromium ferrocyanide is a light greenish colored amorphous solid and gave no X-ray line. The MHCFe were also characterized by TG/DT analysis. The thermogram of CrHCFe, MnHCFe, NiHCFe and ZnHCFe showed a mass loss corresponding to nearly 2.28, 0.55, 0.74 and 2.45 water molecules, respectively. The CHNS analysis data are shown in Table 1. Results of elemental analysis affirm that experimental values are in good agreement



Element	Wt%	At%
CK	38.45	61.94
NK	12.87	17.74
OK	02.70	02.84
MnK	25.57	10.48
FeK	20.41	02.99
Matrix	Correction	ZAF

Fig. 1. FE-SEM image for MnHCFe.

with theoretical value. From the XRD, CHN analysis, TG/DTA, the closest molecular formula of the synthesized MHCFe complexes is as follows.

1. $Cr_2[Fe(CN)_6]{\cdot}2.28H_2O$
2. $Mn_2[Fe(CN)_6]{\cdot}0.55H_2O$
3. $Ni_2[Fe(CN)_6]{\cdot}0.74H_2O$
4. $Zn_2[Fe(CN)_6]{\cdot}2.59H_2O$

Table 1
Carbon, Nitrogen, Hydrogen analysis of MHCFe.

DMC	Carbon (%)	Nitrogen (%)	Hydrogen (%)
CrHCFe	20.17 (19.19)	23.54 (22.31)	0.013 (0.023)
MnHCFe	21.71 (20.87)	25.33 (23.38)	0.003 (0.006)
NiHCFe	21.02 (20.32)	24.52 (24.59)	0.004 (0.005)
ZnHCFe	18.50 (17.75)	21.58 (20.78)	0.013 (0.019)

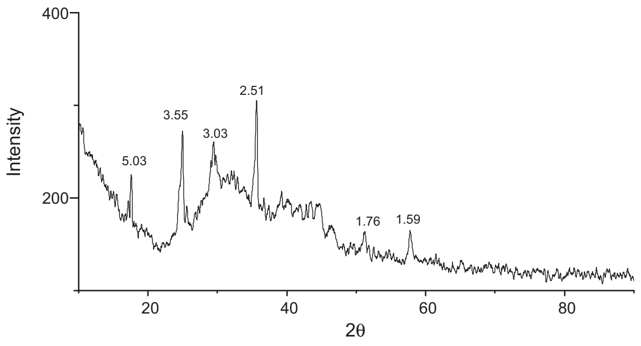


Fig. 2. XRD graph for manganese-ferrocyanide.

3.2. Effects of temperature and catalyst loading on product yields

To test DMCs catalytic activity in the isomerisation of 2′-hydroxychalcones, we have used (*E*)-3-(4-chlorophenyl)-1-(2-hydroxyphenyl) prop-2-en-1-one (Scheme 1). Batch experiments were performed with different DMC catalysts on silica gel at

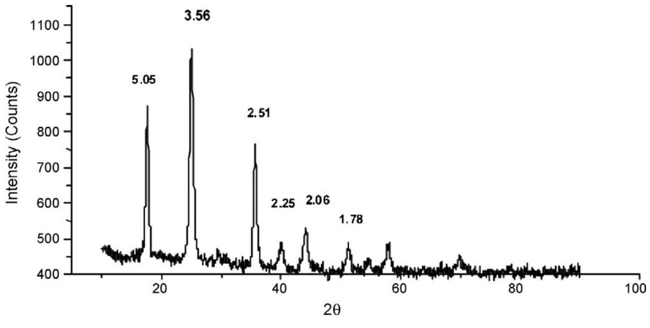
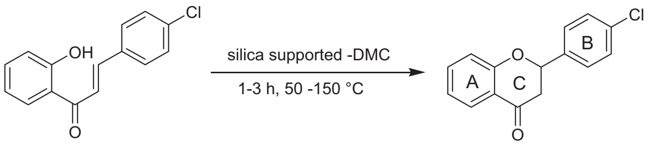


Fig. 3. XRD graph for nickel-ferrocyanide.



Scheme 1. Isomerisation of 2′-hydroxychalcones to flavanone using silica supported DMC.

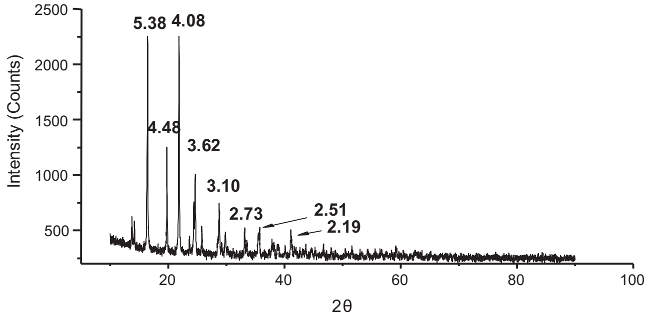


Fig. 4. XRD graph for zinc-ferrocyanide.

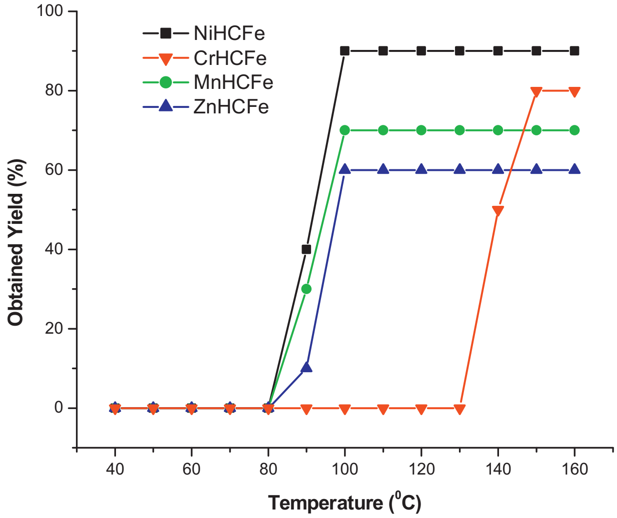


Fig. 5. Effects of temperature on product yields.

different temperature (50–150 °C) and different mol% (5–40 mol%) of catalysts and amount of catalysts and time required.

Temperature effects were studied upto 150 °C by keeping mol% of catalyst constant (10 mol%). We have found that NiHCFe, ZnHCFe, MnHCFe at 100 °C given high yields, but CrHCFe at 150 °C given high yields (Fig. 5). After that keeping temperature as constant at 100 °C for NiHCFe, ZnHCFe, MnHCFe and for CrHCFe 150 °C, we studied the quantity of mol% of catalyst and time required for consuming reactant. We found that NiHCFe at 35 mol% gave 90% yields in 1.15 h; CrHCFe at 35 mol% gave 80% yields in 3 h; MnHCFe at 25 mol% gave 70% yields in 2 h; ZnHCFe at 30 mol% gave 60% yields in 2 h (Fig. 6). Further increasing mol% of catalyst and reaction time has no change in yields. Therefore, among used DMCs, NiHCFe was found highly efficient catalyst in the isomerisation of 2′-hydroxychalcones to flavanones at 100 °C and 35 mol% catalyst loading in 1.15 h.

All the reactions are performed under optimal reaction condition and results are summarized in Table 2. We observed that the substituents on the aromatic rings influenced the product yields. For example, electron releasing substituents such as methyl or methoxy or trimethoxy or *N,N′*-dimethyl on ring B decreases the product yields (30–80%) (Table 2, entries 1, 3, 4, 9, 12 and 16), but the same electron releasing groups on ring A increases the yields (85–86%) (Table 2, entries 7 and 8). Similarly, the presence of electron-withdrawing substituents such as chlorine or bromine on ring B increases the yields (90%) (Table 2, entries 2 and 14), but these groups on ring A decreases the yields (70%) (Table 2, entry 13). Therefore, electron releasing substituents on ring A and electron withdrawing substituents on ring B facilitates the reaction for higher yields.

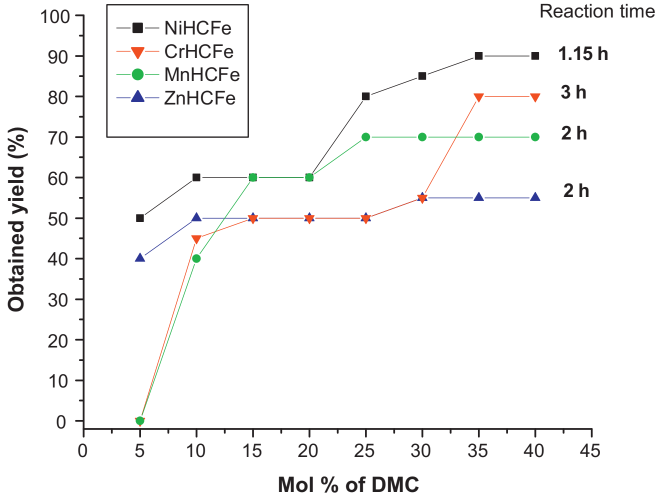


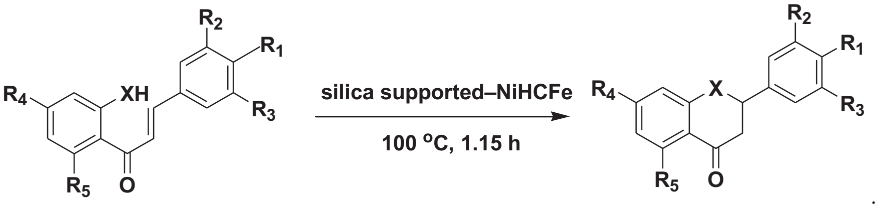
Fig. 6. Effects of mol% of DMCs on yields at 100 °C for Zn-, Ni-, Mn-HCFe and 150 °C for CrHCFe.

In the presence of either silica gel or DMC alone, isomerization reaction failed to occur while DMC in solution in the absence of silica gel gave the products in low yields (5–10%) even after prolonged reaction times and temperature. It has been reported that silica gel or other solid supports such as neutral alumina, HZSM-5 alone catalyse these reactions in relative low yields [21–24]. This confirms that DMC plays an important Lewis acid role in our silica gel supported cyclization reaction. We also tried NiHCFe catalyst for 2′-aminochalcones using dichloromethane solvent at reflux temperature but failed to get the product and further reactant got decomposed might be due to poor host-guest chemistry. Some reactions occur more efficiently in the solid-state than in solution phase because of more tight and regular arrangement of the substrate molecules in the solid-state reaction [50]. Therefore, we tried isomerization of 2′-aminochalcones under solvent free reaction conditions (Table 2, entries 17–20), however got poor yields in this case might be due to poor nucleophilicity of nitrogen. Hence, silica supported DMC is less efficient for the isomerization of 2′-aminochalcones as compared to 2′-hydroxychalcones.

3.3. Proposed reaction mechanism

DMCs might be played an important role in isomerisation of 2′-hydroxychalcones. These catalysts are hydrophobic (no H_2O adsorption at reaction temperatures) and sites are basic in nature (no CO adsorption). Similarly, BrØnsted acid sites are absent (absence of 1546 and 1639 cm^{-1} bands no absorption of pyridine) and so the terminal M^{2+} ion function as Lewis acid sites. Fe in these structures acts as a metal-dispersing agent and a stabilizer of the cyano-bridged complex. Mixed-metal complex of ferrocyanide moiety of Ni^{2+}, Cr^{2+}, Mn^{2+}, Zn^{2+} ions were attached via bridging cyanide ligands (Fig. 7). Cyanide ions act not only as σ-donors (by donating electrons to Fe), but also as π-donors (by chelating to other metal). Electron donation raises the (CN), because electrons are removed from the 5σ orbital which is weakly antibonding in nature. Consequently, the ($C\equiv N$) band shifts to higher frequencies, π-back bonding tends to decrease the ν (CN) because of the electrons enter into the anti-bonding 2pπ orbital. In general, CN^{-1} is a good σ-donor and a poor π-acceptor. Thus (CN) for the complexes is generally higher than the values for free CN^{-1}. IR spectra also suggest that the cyanide ligands are oriented linearly between the divalent Metal and Fe with the C atom coordinated to Fe and N atom coordinated to Ni, Mn, Cr, Zn. Ni-, Cr-, Zn-, Mn-HCFe showed FT-IR band at 2093, 2073, 2083, 2066 cm^{-1} respectively due to ν ($C\equiv N$),

Table 2
Silica gel supported NiHCFe catalyst mediated oxidative cyclization of 2′-hydroxychalcones and 2′-aminochalcones.



Product	XH	R_1	R_2	R_3	R_4	R_5	Yield (%)[a]
1	OH	OCH_3	H	H	H	H	80 (**1b**)
2	OH	Br	H	H	H	H	90 (**2b**)
3	OH	OCH_3	H	OCH_3	H	H	78 (**3b**)
4	OH	OCH_3	OCH_3	OCH_3	H	H	75 (**4b**)
5	OH	H	H	NO_2	H	H	89 (**5b**)
6	OH	OCH_3	H	NO_2	H	H	86 (**6b**)
7	OH	Cl	H	H	OCH_3	H	85 (**7b**)
8	OH	Cl	H	H	OCH_3	OCH_3	86 (**8b**)
9	OH	CH_3	H	H	H	H	80 (**9b**)
10	OH	CH_3	H	H	OCH_3	H	81 (**10b**)
11	OH	CH_3	H	H	OCH_3	OCH_3	83 (**11b**)
12	OH	OH	H	OCH_3	H	H	60 (**12b**)
13	OH	H	H	H	H	NO_2	70 (**13b**)
14	OH	Cl	H	H	H	H	90 (**14b**)
15	OH	H	H	H	H	H	80 (**15b**)
16	OH	$N(CH_3)_2$	H	H	H	H	30 (**16b**)
17	NH_2	Br	H	H	H	H	3 (**17b**)
18	NH_2	OCH_3	H	H	H	H	5 (**18b**)
19	NH_2	NO_2	H	H	H	Br	3 (**19b**)
20	NH_2	OCH_3	H	OCH_3	H	H	2 (**20b**)

[a] Obtained yield.

while $K_4[Fe(C{\equiv}N)_6]$ showed this band at 2039 cm^{-1} due to $\nu(C{\equiv}N)$. IR bands at 1609 and 1450 cm^{-1} indicated the presence of strong Lewis acid sites, while BrØnsted acid sites (IR bands at 1639 and 1545 cm^{-1}) were absent, proving that the DMCs are purely Lewis acid catalysts.

Presumably, the mechanism of the 2′-hydroxychalcones involves the heat-facilitated intramolecular Michael addition of the hydroxy group to the α,β-unsaturated ketone, whereby the essential configuration of both the DMC catalyst and the substrate is secured by their attachment to the silica gel matrix. We have proposed a reaction mechanism for the isomerisation of 2′-hydroxychalcones to flavanones using silica gel supported DMC catalysts (Scheme 2). The importance of silica gel might be related to the silica gel structure which has a complex surface with cavities of different shapes and sizes. The reaction is takes place inside the silica cavities which hold the metal in the appropriate conformation for Lewis acid activation and lower the activation energy of reaction [45]. The solid surface alone is not sufficient, but the acidic sites in DMC catalyst have got a real over the isomerisation of 2′-hydroxychalcones. M^{2+} ion in DMC catalyst are the active sites that activate the carbonyl group of chalcones which is then attacked by —OH group of 2′-hydroxychalcones.

3.4. *Effects of catalyst re-use on product yields*

Reuse of catalysts have many benefits such as economical and eco-friendly reaction, prevention of disposal problems and energy saving. In four different DMCs, NiHCFe catalyst was found excellent for isomerization of 2′-hydroxychalcone to flavanone. At 100 °C and 35 mol% NiHCFe loading reaction gave 90% yields in 1.15 h.

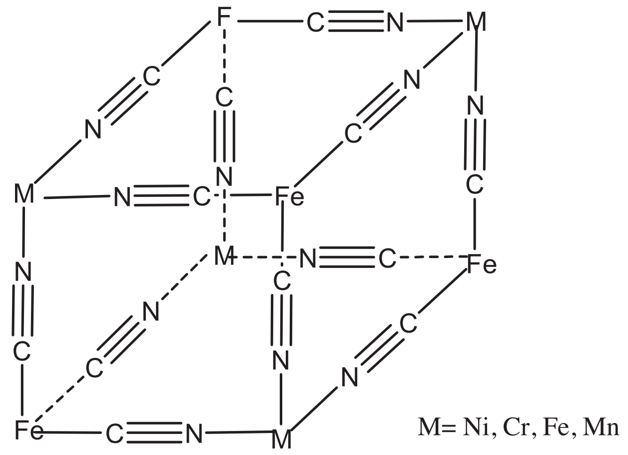
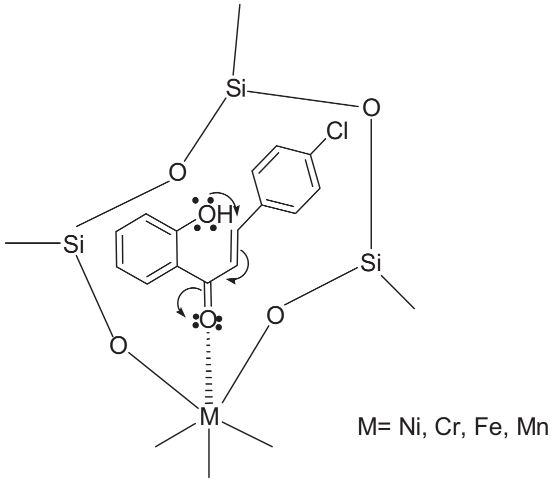


Fig. 7. Structure of metal hexacyanoferrate.



Scheme 2. Proposed mechanism for isomerisation of 2′-hydroxychalcones using silica supported DMCs catalysts.

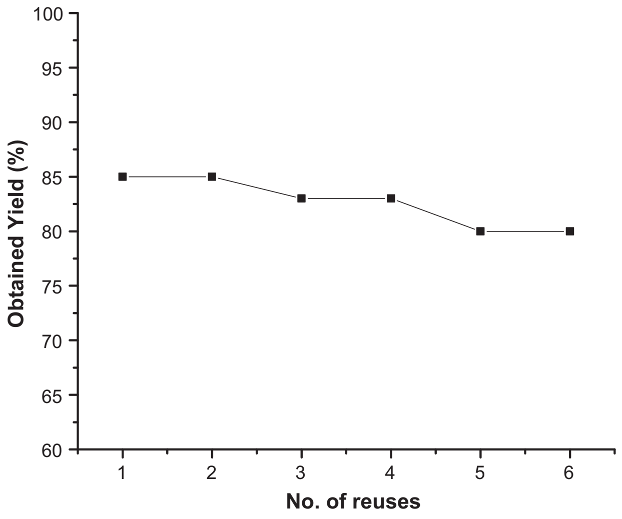


Fig. 8. Effects on yields of catalyst NiHCFe re-use.

Therefore, NiHCFe was examined for the reusability. After reaction completion, the catalyst was filtered, washed with DCM, dried under vacuum and reused many times for the next reaction (Fig. 8). Followed by above reaction condition, it was observed that in first two re-use gave 85% yields, for 3rd and 4th reuse gave 82.5% yields and for 5th and 6th reuse gave 80% yields (Fig. 8). These variations in yields might be due to the loss in work-up.

4. Conclusions

In summary, we reported for the first time Ni-, Mn-, Cr- and Zn-HCFe as a double metal cyanide catalyst in the isomerisation of 2′-hydroxychalcone to flavanone. Among four used catalysts, Lewis-acid, Ni^{2+} ions in double metal cyanide (NiHCFe) exhibited good catalytic activity for the flavanone synthesis in excellent yields under solvent-free condition. The intrinsic catalytic activity of the heterogeneous catalyst is higher than the most of the known catalysts for this reaction. This method has advantages as economical, green, reusable and high yields catalyst.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.03.009.

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