Dolomite (CaMg(CO$_3$)$_2$) as a recyclable natural catalyst in Henry, Knoevenagel, and Michael reactions

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ABSTRACT

Iranian dolomite (CaMg(CO$_3$)$_2$) which consists of double-layered carbonates with Ca^{2+} and Mg^{2+} ions was utilized as a heterogeneous base catalyst in the C—C, C—N, and C—S bond forming reactions via the Henry, Knoevenagel, aza-Michael, and thia-Michael transformations under mild conditions in water. Iranian dolomite has been characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Brunauer Emmett Teller (BET) and XRF chemical analysis, while its basic strength was evaluated by following the Hammett indicators procedure. This water-insoluble natural catalyst demonstrated high activity and was reusable.

1. Introduction

Organic transformations can be made more profitable by use of recoverable natural catalysts and water as the least hazardous chemicals [1]. Therefore, catalytic researches have been recently focused on the use of heterogeneous mineral catalysts such as bentonite, kaolin, apatite, clays, and metal oxides [2–16]. These naturally occurring catalysts efficiently catalyze the organic reactions via adsorption of the starting materials and enhancement of their reactivity. The extra advantages of these catalysts which make them good candidates for green processes are availability, non-volatility, stability, non-toxicity, reusability, and low cost.

Dolomite (CaMg(CO$_3$)$_2$) is a very cheap water insoluble sedimentary carbonate rock which consists of the Ca^{2+} and Mg^{2+} ions with double-layered carbonates [17–19]. Although dolomite has various structural characteristics, it is best known for its saddle-shaped crystals that help to its high stability at ~350 °C [18]. However, MgCO$_3$ part of dolomite decomposes to CO$_2$ and MgO at 350–545 °C, while decomposition of the CaCO$_3$ fraction of dolomite occurs at 825 °C. Thus calcined dolomite can be considered as a composite mixture of MgO and CaO with higher base strength than uncalcined dolomite with carbonate base. This heterogeneous catalyst has been recently used in the production of biodiesels via transesterification reaction of canola oil with methanol [19]. We

have considered this natural base catalyst for promotion of the C—C, C—N, and C—S bond forming reactions in aqueous media.

Henry and Knoevenagel condensations [20–23] are two important C—C bond forming reactions that produce Michael acceptors as key synthetic intermediates. Both reactions are routinely performed via the base-catalyzed aldol-type addition of CH active to carbonyl compounds along with the production of nitroalkanols and electron-deficient alkenes [22–24]. Due to the serious competition of aldol-condensation, Canizzaro and Nef-type reactions, polymerization, and dehydration of nitroalkanols with Henry and Knoevenagel reactions, several modifications have been developed to increase their chemo- or regio-selectivity [24–29].

Aza- and thia-Michael additions are known synthetic tools for the creation of C—N and C—S bonds via nucleophilic reaction of amines and thiols with electron-deficient alkenes as Michael acceptors [30–35].

Due to the benefits of dolomite as a naturally occurring heterogeneous base catalyst, in continuation of our recent researches [36–40], herein we report the use of dolomite as a new natural recyclable catalyst in the Henry, Knoevenagel, and Michael reactions in water (Scheme 1).

2. Experimental

2.1. General

Chemicals were commercially available and used without further purification unless otherwise stated. The Iranian dolomite

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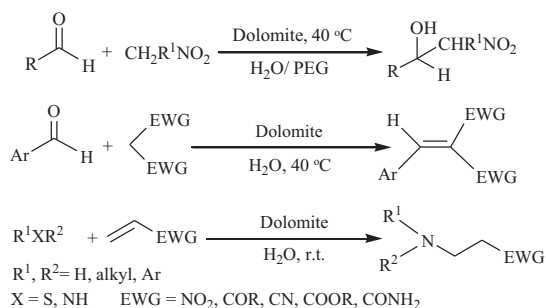
Scheme 1. Dolomite-catalyzed Henry, Knoevenagel, and Michael reactions.

with purity >98.5% was extracted from Tabas mine, by Kansaran Binaloud Co., Ltd, located in Mashhad, Iran. ^{1}H NMR and ^{13}C NMR spectra were recorded at 250 or 500 MHz and 62.9 or 125 MHz, respectively. Chemical shifts are given in ppm with respect to internal TMS. IR measurements were performed on a Brucker FT-IR spectrometer. Melting points are uncorrected. All products showed the same physical, analytical, and spectral data with those reported in the literature.

2.2. Characterization of catalyst

The extracted Iranian dolomite was finely grinded in an agate mortar as a gray-white powder, washed with hot water, and calcined at 300 °C for 3 h. The chemical composition of Iranian dolomite was determined by XRF analysis and its structure was confirmed by FT-IR spectroscopy and X-ray diffraction analysis (purity > 98.5%). Basic strength and the surface area of the Iranian dolomite was evaluated by following the Hammett indicator procedure and BET method, respectively.

2.3. General experimental procedure for the Henry reaction

A mixture of aldehyde (5 mmol), nitroalkane (10 mmol), and dolomite (0.5 g, ~2.5 mmol) in 50% polyethyleneglycol and water (PEG-400/H_2O (5 mL)) was stirred at ~40 °C for the given times (Tables 2 (entry 11) and 3). Progress of the reaction was followed by TLC and after the completion of the reaction, EtOAc (50 mL) was added and catalyst was filtered off. The filtrate was washed with saturated aqueous $NaHSO_3$ (for removing the remained aldehyde, if necessary) and dried over Na_2SO_4. The product was isolated by evaporation of the solvent and purified in some cases by flash chromatography (hexane:EtOAc, 80:20) to afford the pure product.

2.4. General experimental procedure for the Knoevenagel condensation

To a mixture of activated methylene compound (2 mmol) and dolomite (0.2 g) in H_2O (3 mL) was added aldehyde (2 mmol) and the mixture was stirred at ~40 °C for elevated time (Table 4). After totally consumption of aldehyde (TLC monitoring), the reaction mixture was diluted with ethyl acetate and filtered to remove dolomite. The filtrate was concentrated to give the tri-substituted alkene products.

2.5. General experimental procedure for the Michael-addition reactions

To a mixture of amine (or thiol) (2 mmol) and dolomite (0.2 g, ~50 mol%) in water (2 mL) was added Michael-acceptors such as nitrostyrene, acrylonitrile, methyl vinyl ketone, methyl methacrylate, cyclohexenone, or acryl amide (2 mmol). The mixture was stirred at room temperature for the given times (Table 5). After

completion of the reaction (TLC monitoring), ethyl acetate (10 mL) was added and dolomite was removed by filtration. The product was isolated after evaporation of the solvent.

The obtained nitroalkanols, alkenes, and Michael reaction products were known and characterized by comparison of their physical or spectral data with the authentic samples or with those of reported earlier.

2.6. Reusability of catalyst

Dolomite was recovered from the reaction of nitromethane and benzaldehyde after washing with ethyl acetate. Elemental analysis of the used catalyst was the same as preliminary dolomite that show the stability of dolomite structure under reaction conditions. Despite of the absorption of water by recycled dolomite (very broad OH stretching of hydrated carbonate of dolomite at 2600–3600 cm^{-1} in the FT-IR spectrum), it was reused three times in the same Henry reaction in water and no decreasing of the yields was observed.

Similarly, the recycled dolomite from the Knoevenagel condensation of malononitrile and benzaldehyde in water was used in the second run of the reaction and no significant loss of activity for the reused catalyst was observed. The filtered dolomite from Michael-addition of aniline to nitrostyrene was also washed with ethyl acetate and EtOH. After drying at ~300 °C, the recycled catalyst was used in the further runs but the yield of product was reduced (>10% than the original catalyst) in the third run of reaction.

2.7. Representative data for the selected compounds

2.7.1. 1-(2,4-Dichloro-phenyl)-2-nitro-ethanol (Table 3, entry 15)
Thick oil, 91% yield, FT-IR: ν_{max} (KBr) 3502, 1555 and 1381 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$) δ: 3.26 (br s, 1H, OH), 4.42 (dd, 1H, $J_1 = 13.6, J_2 = 9.4$ Hz, CH_2), 4.67 (dd, 1H, $J_1 = 13.6, J_2 = 2.4$ Hz, CH_2), 5.79 (d, 1H, $J = 9.4$ Hz, CHOH), 7.24–7.48 (m, 2H), and 7.61 (d, 1H, $J = 8$ Hz) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$) δ: 67.8, 79.4, 128.4, 129, 129.9, 132.5, 134.5, and 135.6 ppm. EIMS (probe) 70 eV, m/z: 235, 217, 188, 175, 147, 145, 46, 30, and 29.

2.7.2. (E)-2-(4-chlorophenyl)-1-nitro-1-cyanoethene (Table 4, entry 3) [41]
Pale orange powder, Mp = 115–116 °C. FT-IR: ν_{max} (KBr) 3053, 2943, 2230, 1615, 1590, 1548, 1426, 1330, 1220, 1067, 933, 947, 819, 771, and 621 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.50–8.00 (m, 4H, H$_{aromatic}$), and 8.64 (s, 1H, H$_{vinyl}$) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$) δ: 111.0, 123.5, 126.5, 129.5, 133.0, 140.5, and 147.0 ppm.

2.7.3. (E)-2-furyl-1-nitro-1-cyanoethene (Table 4, entry 12) [41]
Pale brown solid, Mp = 147–149 °C. FT-IR: ν_{max} (KBr) 3083, 2953, 2235, 1612, 1595, 1548, 1426, 1335, 1228, 1067, 950, 822, 775, and 651 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ 6.80–7.90 (m, 3H, H$_{aromatic}$), and 8.42 (s, 1H, H$_{vinyl}$) ppm. ^{13}C NMR (62.5 MHz, CDCl$_3$) δ: 111.5, 116.0, 120.0, 129.5, 133.5, 145.5, and 152.5 ppm.

2.7.4. 1,1-Dicyano-2-(pyridine-4-yl)ethylene (Table 4, entry 13)
White needles (EtOH:H_2O), Mp = 100–101 °C. FT-IR: ν_{max} (KBr) 3023, 2933, 2233, 1610, 1590, 1548, 1416, 1403, 1236, 1219, 1067, 933, 947, 819, 771, and 621 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.69 (d, $J = 5.3$ Hz, 2H, H$_{aromatic}$), 7.83 (s, 1H, H$_{vinyl}$), and 8.88 (d, $J = 5.3$ Hz, 2H, H$_{aromatic}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ: 89.0, 111.7, 112.9, 123.0, 137.4, 151.9, and 158.0 ppm.

Table 1
Chemical analysis of Iranian dolomite.

Entry	Component	Percentage (%)
1	Mg	21.16
2	Ca	30.64
3	CO$_3$	46.71
4	Other components (Fe$_2$O$_3$, SiO$_2$, K$_2$O, TiO$_2$, Na$_2$O, MnO, Al$_2$O$_3$, P$_2$O$_5$)	1.49

2.7.5. 4-(Methylphenylamino)-butan-2-one (Table 5, entry 9) [30]

93% yield. FT-IR: ν_{max} (KBr) 3050, 2920, 1712 (C=O) 1590, 1420, 1380, 680, and 750 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ 2.30 (s, 3H, MeCO), 2.65 (t, 2H, CH$_2$), 2.88 (s, 3H, MeN), 3.6 (t, 2H), 6.50–6.80 (m, 3H, H$_{aromatic}$), and 7.12–7.24 (m, 2H, H$_{aromatic}$) ppm. ^{13}C NMR (62.5 MHz, CDCl$_3$) δ: 30.6, 38.5, 40.5, 47.3, 112.4, 116.5, 129.3, 148.6, and 208.0 ppm.

2.7.6. 3-(4-Nitrophenylsulfanyl)-cyclohexanone (Table 5, entry 17) [31]

Yellow needles (EtOH:H$_2$O), Mp = 70–71 °C. FT-IR: ν_{max} (KBr) 1715 (C=O), 1505 and 1340 (NO$_2$) cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.80–1.90 (m, 2H, CH$_2$), 2.10–2.25 (m, 2H, CH$_2$), 2.40–2.50 (m, 3H), 2.76–2.80 (dd, J_1 = 14.4, J_2 = 4.5 Hz), 3.70–3.75 (m, 1H), 7.40 (d, J = 8.3 Hz, 2H, H$_{aromatic}$), and 8.10 (d, J = 8.3 Hz, 2H, H$_{aromatic}$). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ 24.3, 31.20, 41.0, 44.8 47.50, 124.3, 129.2, 144.3, 146.0, and 207.0 ppm.

3. Results and discussion

3.1. Identification of dolomite

The purity and chemical composition of the finely grinded Iranian dolomite as a gray-white powder was determined according to the qualitative and quantitative elemental analysis and material characterization by X-ray fluorescence assessment (XRF). The result of XRF analysis is given in Table 1.

As results indicate, the purity of the finely powdered mineral dolomite was higher than 98%.

The characteristic bands in FT-IR spectra of dolomite confirm the presence of carbonyl of carbonate as a broad band at 1434 cm^{-1} [17]. The two dolomite diagnostic FT-IR absorption bands at 2626 cm^{-1} and 730 cm^{-1} are respected to the non-fundamental combination frequencies and in plane bending mode of CO$_3^{2-}$ part of dolomite. A little adsorbed surface water was evidenced by the presence of the broad OH stretching of hydrated carbonate at 2500–3500 cm^{-1} for the Iranian dolomite.

Crystalline structure of the Iranian dolomite was determined by powder X-ray diffraction (XRD). The peaks positioned at various 2θs of catalyst were compatible with those in the standard XRD pattern of CaMg(CO$_3$)$_2$ (1999 JCPDS file No. 36-0426). According to the XRD pattern, other carbonate phases such as NaHCO$_3$ or Na$_2$CO$_3$ were not observed together with the dolomite phase [18]. The surface area of the Iranian dolomite was obtained using the BET method and was found 12.8 m^2/g.

Basic strength (H_-) of the Iranian dolomite was evaluated as 7.1 following a previously reported Hammett indicator procedure in the studies of Ilgen [19]. For this measurement, under nitrogen atmosphere, 50 mg of catalyst was stirred with appropriate volumes of methanol solutions of Hammett indicators including bromothymol blue (H_- = 7.2), phenolphthalein (H_- = 9.8), dinitroaniline (H_- = 15.0) and nitroaniline (H_- = 18.4) and left to equilibrate for 2 h, after which no further color changes were observed. The color on the catalyst was then noted. The stronger base than the weakest indicator demonstrates a color change, but weaker than the strongest indicator shows no color change.

Table 2
Optimization of the Henry reaction of benzaldehyde with nitromethane.
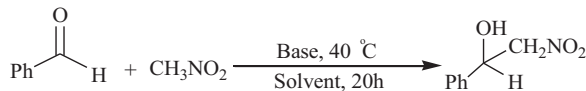
Entry	Base/solvent[a]	Yield (%)[b]
1	ZnO/H$_2$O	15
2	CaO/H$_2$O	30[c]
3	KF-Alumina/H$_2$O	75[c]
4	Amberlyst-A-29/H$_2$O	20
5	Molecular sieves/H$_2$O	15
6	Amberlyst-R-900/H$_2$O	15
7	Et$_3$N-SiO$_2$/H$_2$O	75[c]
8	4-PVP/H$_2$O	15
9	NaHCO$_3$-Bentonite/H$_2$O	75[c]
10	Dolomite/H$_2$O	70
11	Dolomite/H$_2$O/PEG-400	90
12	Dolomite/EtOH	30[c]
13	Dolomite/CH$_3$CN	15[c]
14	Dolomite/MeNO$_2$ (Excess)	15[c]
15	Dolomite/H$_2$O/PEG-400	60[d]
16	None/H$_2$O/PEG-400	<10
17	CaCO$_3$/H$_2$O/PEG-400	70[c]
18	MgCO$_3$/H$_2$O/PEG-400	75[c]
19	CaO/H$_2$O/PEG-400	67[c]
20	MgO/H$_2$O/PEG-400	70[c]

[a] A mixture of benzaldehyde (1 mmol), nitromethane (2 mmol) and base (~0.5 mmol) was stirred at ~40 °C.
[b] Isolated yield.
[c] 2-Nitro-1-phenylethanol was formed together with the nitrostyrene, benzoic acid, and 1,3-diniro-2-phenyl-propane.
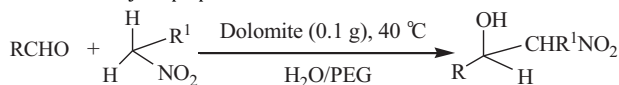[d] 1 mmol of MeNO$_2$.

3.2. Dolomite-catalyzed Henry and Knoevenagel reactions in water

To determine the catalytic efficacy of dolomite, the Henry reaction of nitromethane and benzaldehyde was studied comparatively with various basic catalysts under various conditions (Table 2).

As results indicate the yield of 2-nitro-1-phenylethanol was higher in the presence of dolomite in aqueous media (entries 3, 7, 10, 15 and 17–20), especially when PEG-400 was used to increase the low solubility of organic compounds in the aqueous media of reaction (Table 2, entry 11). Performing the dolomite-catalyzed Henry reaction in other solvents led to the formation of three side products which were isolated by column chromatography on silica gel (hexane:EtOAc, 8:1) as nitrostyrene, benzoic acid, and 1,3-dinitro-2-phenyl-propane. The better reaction yield in water/PEG-400 mixture can be rationalized by the assistance of PEG as a phase transfer catalyst, a co-solvent, or a micelle maker with carbonate part of dolomite in its saddle-shape crystalline structure. These reasons were supported by the higher observed selectivity of reaction with dolomite (least side reactions) than simple calcium and magnesium carbonates or oxides (Table 2, entries 17–20). Thus, the optimal conditions for dolomite-catalyzed Henry reaction were 0.1 g or ~0.5 mmol of catalyst in water/PEG-400 mixture.

The same optimization was made for the Knoevenagel condensation of benzaldehyde and malononitrile at various dolomite loading in water at room temperature and again the 0.1 g (~50 mol%) of dolomite was chosen as the best amount of catalyst. The scope of dolomite-catalyzed Henry reaction and Knoevenagel condensation at the optimized conditions were illustrated in Tables 3 and 4. The clean reactions with high yields of desired products for a variety of electron-withdrawing and electron-releasing substituted aldehydes and methylene compounds are advantages of these reactions.

Table 3
Dolomite catalyzed preparation of nitroaldoles.

$$RCHO \ + \ \overset{\overset{H}{|}}{\underset{\underset{NO_2}{|}}{H}} R^1 \xrightarrow[H_2O/PEG]{Dolomite\ (0.1\ g),\ 40\ ^\circ C} \ \overset{OH}{\underset{R}{\overset{|}{\underset{|}{C}}}}\overset{}{\underset{H}{CHR^1NO_2}}$$

Entry	R	R^1	Time (h)	Yield (%)[a]
1	n-Propyl	H	10	90
2	n-Propyl	CH$_3$	12	75
3	PhCH$_2$CH$_2$	H	2	90
4	2-O$_2$NC$_6$H$_4$	H	2.5	95
5	2-O$_2$NC$_6$H$_4$	CH$_3$	6	93[b]
6	3-O$_2$NC$_6$H$_4$	CH$_3$	18	90[b]
7	3-O$_2$NC$_6$H$_4$	H	18	93
8	4-O$_2$NC$_6$H$_4$	H	18	95
9	4-O$_2$NC$_6$H$_4$	CH$_3$	18	90[b]
10	2-ClC$_6$H$_4$	H	18	86
11	4-ClC$_6$H$_4$	H	18	85
12	4-CH$_3$C$_6$H$_4$	H	20	70
13	4-MeOC$_6$H$_4$	H	18	68
14	4-OHC$_6$H$_4$	H	20	75
15	(3,4-dichlorophenyl)	H	18	91

[a] Isolated yield.
[b] Thero:erythro (100:1).

Reaction of 2-hydroxybenzaldehyde with malononitrile yielded a pale yellow crystalline compound with Mp = 163–165 °C and showed a characteristic NH stretching in its FT-IR spectra. According to the spectral and physical data, sequential Knoevenagel condensation and internal nucleophilic attack of OH to the CN group led to 2-imino-2H-1-benzopyran-3-carbonitrile [42] in 82% yield (Scheme 2).

An advanced comparison between the results of dolomite-catalyzed Henry and Knoevenagel reactions confirm that Henry's nitroalkanols did not dehydrate in the presence of dolomite, while dehydration of Knoevenagel alkanols led to tri-substituted alkenes under similar conditions. Driving force for this dehydration is
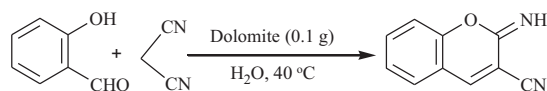
Scheme 2. Dolomite-catalyzed Knoevenagel reaction of salicylaldehyde.

more acidity of the α-hydrogens attached to carbon with two electron-withdrawing groups (CN, NO$_2$, and CO) than carbon attached to NO$_2$ in Henry's nitroalkanols. Advantageously, dolomite is a mild enough base to differentiate between these two kinds of α-hydrogens. As supposed in Scheme 3, dolomite acts as a dual activator of CH$_2$ and C=O groups via chair like intermediates which carbonate part of dolomite is responsible for the abstraction of α-hydrogens, whereas Mg^{2+} and Ca^{2+} are responsible for the activation of coordinated carbonyl group. This led to the more susceptibility of the carbonyl group toward the nucleophile attack of the carbanion preformed by abstraction of α-hydrogen with carbonate of dolomite.
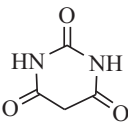
Dolomite-catalyzed condensation of nitromethane or malononitrile with acetophenone as a less electrophile and more hindered carbonyl group gave no product under similar conditions and confirmed again the chemoselectivity of dolomite in these reactions. Condensation of malononitrile with acetic anhydride, benzoyl chloride, and acetyl chloride were also attempted but only acetyl chloride reacted with malononitrile at ∼40 °C to give a mixture of β-ketonitrile and β-ketoamide.

3.3. Dolomite catalyzed Michael-type addition reactions in water

In order to verify the versatility of dolomite as a natural catalyst, we examined dolomite-catalyzed aza- and thia-Michael addition reactions of various N- and S-nucleophiles to Michael-acceptors prepared from dolomite-catalyzed Henry and Knoevenagel reactions (Table 5).
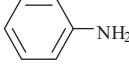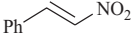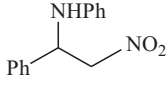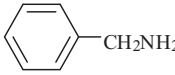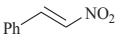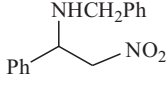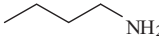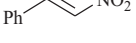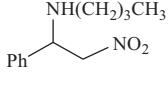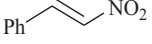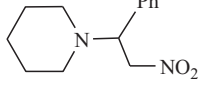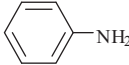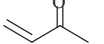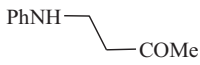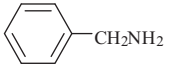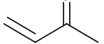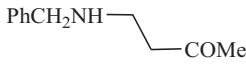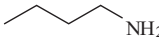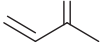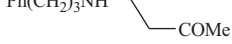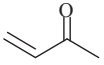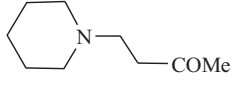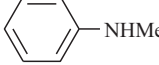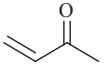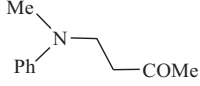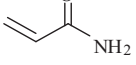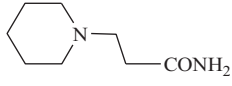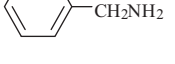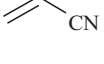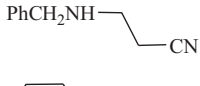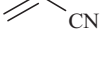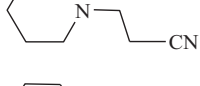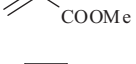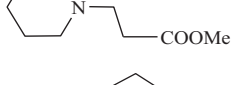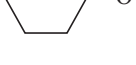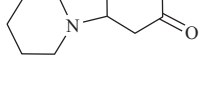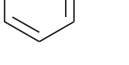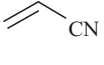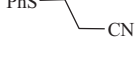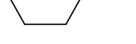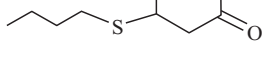
The results clearly reveal that the presence of dolomite as a reaction promoter is essential for the efficiency of process. A reasonable account for this promotion is affording a mild basic media

Table 4
Dolomite catalyzed preparation of tri-substituted alkenes.

$$\underset{Ar}{\overset{O}{\parallel}}\overset{}{C}{-}H \ + \ EWG{\frown}EWG \xrightarrow[H_2O,\ 40\ ^\circ C]{Dolomite\ (0.1\ g,\ \sim 50\ mol\%)} \ \overset{H}{\underset{Ar}{\diagdown}}C{=}C\overset{EWG}{\underset{EWG}{\diagup}}$$
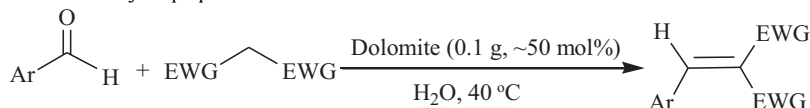
Entry	Ar	Substrate	Time (h)	Yield (%)[a]	Mp (°C)[b] [ref.]
1	Ph	NCCH$_2$CN	1	93	84–86 [29]
2	4-ClC$_6$H$_4$	NCCH$_2$CO$_2$Et	2.5	91[c]	91–92 [42]
3	4-ClC$_6$H$_4$	NCCH$_2$NO$_2$	0.5	96[c]	116–118 [41]
4	4-O$_2$NC$_6$H$_4$	NCCH$_2$CN	0.5	94	162–163 [43]
5	4-O$_2$NC$_6$H$_4$	NCCH$_2$CO$_2$Et	2	90[c]	169–170 [43]
6	4-MeOC$_6$H$_4$	NCCH$_2$CN	1.5	91	116–117 [42]
7	4-MeOC$_6$H$_4$	NCCH$_2$CO$_2$Et	2.5	85[c]	80–81 [42]
8	4-MeC$_6$H$_4$	NCCH$_2$CN	1.5	92	129–130 [42]
9	2-O$_2$NC$_6$H$_4$	NCCH$_2$CO$_2$Et	0.5	95[c]	139–141 [29]
10	4-HOC$_6$H$_4$	NCCH$_2$CN	1.5	90	188–189 [42]
11	2-Furyl	NCCH$_2$CN	1	92	72–73 [42]
12	2-Furyl	NCCH$_2$NO$_2$	0.5	96[c]	125–127 [42]
13	4-Pyridyl	NCCH$_2$CN	1	90	100–101
14	2-Pyridyl	NCCH$_2$CN	0.5	_[d]	_[d]
15	Ph	(barbituric acid)	1.2	92	257–259 [42]

[a] Isolated yields.
[b] These values are comparable with those reported in the literature.
[c] Only E-isomer was obtained.
[d] A polymeric product was obtained.

Table 5
Dolomite-catalyzed conjugated addition of amines or thiols to Michael acceptors in water.

Entry	Nucleophile	Michael acceptors	Time (min)	Product[a]	Isolated yield (%)
1	$C_6H_5NH_2$ (aniline)	$PhCH=CHNO_2$	30	Ph–CH(NHPh)–CH$_2$NO$_2$	93
2	$C_6H_5CH_2NH_2$	$PhCH=CHNO_2$	20	Ph–CH(NHCH$_2$Ph)–CH$_2$NO$_2$	95
3	$CH_3CH_2CH_2CH_2NH_2$	$PhCH=CHNO_2$	20	Ph–CH(NH(CH$_2$)$_3$CH$_3$)–CH$_2$NO$_2$	95
4	piperidine (NH)	$PhCH=CHNO_2$	15	N-piperidinyl-CH(Ph)–CH$_2$NO$_2$	98
5	$C_6H_5NH_2$	methyl vinyl ketone	15	PhNH–CH$_2$CH$_2$–COMe	92
6	$C_6H_5CH_2NH_2$	methyl vinyl ketone	10	PhCH$_2$NH–CH$_2$CH$_2$–COMe	94
7	$CH_3CH_2CH_2CH_2NH_2$	methyl vinyl ketone	30	Ph(CH$_2$)$_3$NH–CH$_2$CH$_2$–COMe	93
8	piperidine (NH)	methyl vinyl ketone	5	N-piperidinyl–CH$_2$CH$_2$–COMe	96
9	C_6H_5NHMe	methyl vinyl ketone	30	Me,Ph–N–CH$_2$CH$_2$–COMe	93
10	piperidine (NH)	acrylamide ($CH_2=CHCONH_2$)	20	N-piperidinyl–CH$_2$CH$_2$–CONH$_2$	91[b]
11	$C_6H_5CH_2NH_2$	acrylonitrile ($CH_2=CHCN$)	60	PhCH$_2$NH–CH$_2$CH$_2$–CN	91
12	piperidine (NH)	acrylonitrile ($CH_2=CHCN$)	30	N-piperidinyl–CH$_2$CH$_2$–CN	95
13	piperidine (NH)	methyl methacrylate ($CH_2=C(CH_3)COOMe$)	30	N-piperidinyl–CH$_2$CH$_2$–COOMe	93
14	piperidine (NH)	cyclohex-2-enone	30	3-piperidinyl-cyclohexanone	88
15	C_6H_5SH (thiophenol)	acrylonitrile ($CH_2=CHCN$)	30	PhS–CH$_2$CH$_2$–CN	94
16	$CH_3CH_2CH_2CH_2SH$	cyclohex-2-enone	30	3-(butylthio)-cyclohexanone	90

[a] All products were known and characterized by comparison of their spectral data with those of reported.
[b] A mixture of products contain β-amino carbamide were formed.

A: Chair-like transition state for dolomite-catalyzed Henry reaction.
The acidity of labeled hydrogen by star is not sufficient.

M: Mg^{2+}, Ca^{2+}
X: Heteroatom (N or O) of electron-withdrawing group (EWG = CN, COOEt, NO_2, and CO)
B: Chair-like transition state for dolomite-catalyzed Knoevenagel reaction.
The acidity of labeled hydrogen by star is sufficient to abtract by dolomite.
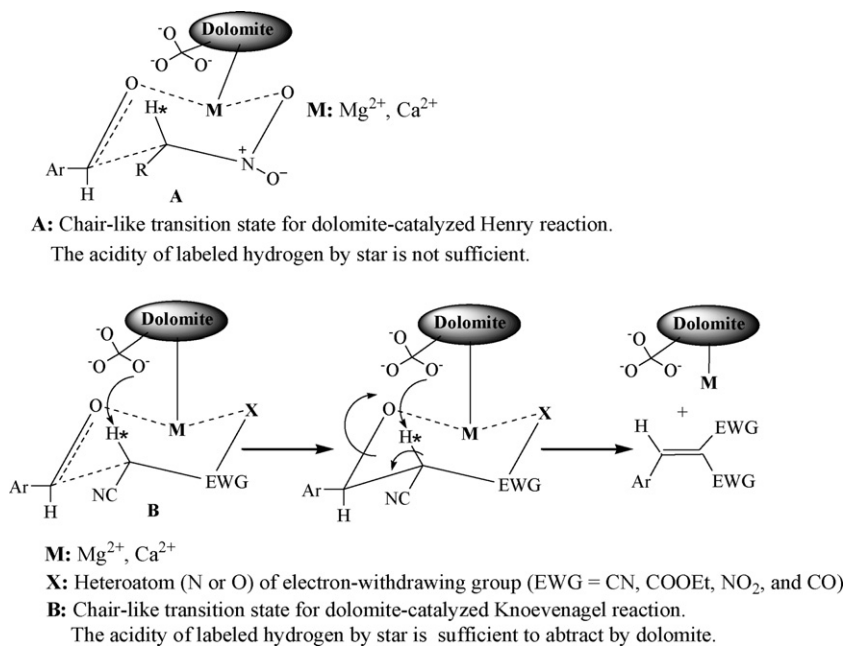
Scheme 3. Proposed mechanism for dolomite-catalyzed condensation reactions.

by dolomite for dual activation of nucleophiles and conjugated double bonds to C=O group. The nucleophilicity of NH- or SH-bond increases via the hydrogen bonding with carbonate part of dolomite [44] and the susceptibility of the conjugated double bonds enhanced by coordination of the C=O group to Mg^{2+} and Ca^{2+} of dolomite.

No transamidation or replacement of the ester group by amine was observed under these mild conditions and the reactivity of different Michael acceptors were strongly related to the nature and power of their electron-withdrawing groups. Therefore, the aza-Michael addition of N-nucleophiles to nitrostyrene occurred in higher yield than acrylamide (Table 5, entries 1–4).

Moreover, the chemoselectivity of reaction was demonstrated by the competitive dolomite-catalyzed aza-Michael addition of aniline and benzyl amine with nitrostyrene. This led to the formation of N-benzyl-2-nitro-1-phenylethanamine in 94% yield in water. Reaction of methyl vinyl ketone with a 1:1 mixture of piperidine and benzylamine was also afforded the 4-(piperidin-1-yl)butane-2-one in 93% yield (Scheme 4).

The synthesis of 1,3-dinitro-2-phenyl-propane was also attempted by addition of large excess of nitromethane to nitrostyrene in the presence of dolomite (0.2 g, ~1 mmol) under reflux conditions (Scheme 5).

The recyclability of dolomite was next examined for the Henry reaction of benzaldehyde with nitromethane, Knoevenagel
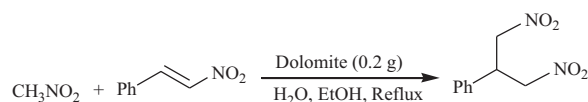
**Scheme 5.** Michael addition of nitromethane to nitrostyrene.

condensation of malononitrile with benzaldehyde, and Michael addition of benzylamine to nitrostyrene in water. In all cases, the filtered and washed catalyst was dried at room temperature. The FT-IR spectra and XRF analysis of the recycled and re-dried dolomites were the same as fresh ones. The regenerated dolomites were then subjected to the further reaction runs. The yields of the first Henry and Knoevenagel experiments were similar with three subsequent reaction runs in the presence of recycled dolomite. Even in the Michael addition after two runs, catalytic activity of the recycled dolomite was less than fresh catalyst. The loss of activity is may be related to the deactivation of catalyst by coke formation from both nitrostyrene and benzylamine during the Michael addition reaction at room temperature.

4. Conclusion

In summary, we have developed a green advance to Henry, Knoevenagel, and Michael reactions in water for the preparation of nitroalkanols, tri–substituted alkenes, β-amino and β-thio substituted carbonyl compounds in the presence of Iranian dolomite as a new heterogeneous natural catalyst. This catalyst benefits from the chemoselectivity, non-toxicity, environmental safety, simple handling, reusability, and versatility for various organic transformations in a range of substrates.

Acknowledgment
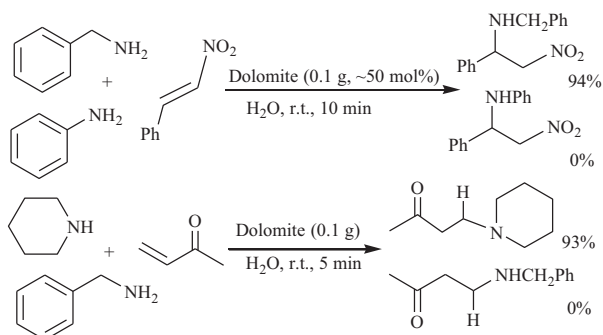
Scheme 4. Chemoselectivity of dolomite-catalyzed Michael-reactions.

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.2012.08.027.

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