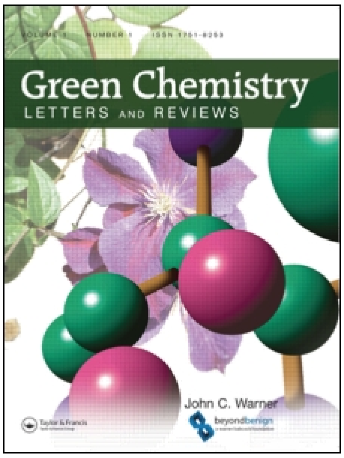

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ORIGINAL ARTICLE

The efficient synthesis of carbon–carbon double bonds via Knoevenagel condensation using red mud packed in a column

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Red mud (RM) is generated as a by-product during the production of alumina from bauxite ore. In this study, RM packing in a column is used as a catalyst for carbon–carbon double bond formation via Knoevenagel condensation. The reactants are added to the top of the column and then eluted with solvent. The products are collected in high yields and short time. RM packed in a column eliminates a catalyst separation step from the reaction mixture in this work.

Keywords: Red mud; packed column; Knoevenagel condensation; C=C bond formation

Introduction

Bauxite residue, also known as red mud (RM), is the major solid waste produced in the process of alumina extraction from bauxite ore (Bayer process) (*1*). The amount of RM generated varies greatly depending on the type and grade of bauxite, ranging from 1 to 1.6 tons per ton of produced alumina (*2*). The major contaminates of RM are the oxides of iron, silicon, aluminum and titanium. Elements, such as zinc, phosphorous, nickel and vanadium, are found in trace amounts. Table 1 shows the wide range of chemicals found in RM.

In many alumina plants, the RM is typically stockpiled on-site, resulting in the accumulation of ever increasing amounts of RM at the plant site (*2*). As RM is generated as a by-product at high scale, the reuse and recovery of RM is an important goal. Work is being conducted to develop useful products from the RM. For example, there are reports of using RM as a raw material in the production of detergent-grade zeolite 4A (*5*), special cement (*6*), inexpensive building brick (*7*), and ceramic (*8*). RM is used for some chemical processes, such as producing hydrogen gas from coke (*9*), absorbing compounds such as arsenic (*10*), phosphate (*11*), nitrate (*12*), chromate (*13*), boron (*14*), fluoride (*15*), cadmium, lead, copper (*16*), phenol (*17*) and dye (*18*) from wastewater, as well as absorbing salt produced from sea water (*19*). Additionally, the catalytic activity of RM is known for the hydrogenation of organic compounds (*20*), and the hydrodechlorination of tetrachloroethylene (*21*). It has been found to degrade mixtures of municipal waste plastic, heavy vacuum gas oil and waste mineral oil to fuel oil (*22*). In this paper, we report the use of RM as an efficient catalyst for C=C bond formation via Knoevenagel reactions which have been commonly employed in the synthesis of numerous specialty chemicals and chemical intermediates (*23*).

The Knoevenagel condensation is a useful reaction for the generation of double bonds from a carbonyl compound and an active methylene compound. Many homogeneous catalysts have been used to promote Knoevenagel reactions, such as triethylamine, pyridine–$TiCl_4$, secondary amines, etc. (*24*). More recently, the uses of heterogeneous basic catalysts have been employed to facilitate the separation of the catalyst from the reaction media. Furthermore, in many cases the catalyst may be reused. Metal oxides supported on silica-gel, barium hydroxide, zeolites, montmorillonite, magnesium and aluminum oxides, hydrotalcite (*25*), Cs-MCM-41 (*26*), modified silicagel (*27*), and, more recently, Ga/Al-containing layered double hydroxides (*28*), are just a few examples of effective materials which may be used for the Knoevenagel condensation. In some cases, the reaction can be achieved under dry conditions, thus decreasing both the cost of the synthesis and the amount of waste flow (*29*).

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Table 1. RM chemical composition.

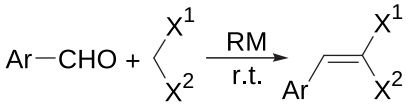
Contaminates	Chemical form (*3*)	Content (W%) (*4*)
Fe_2O_3	Hematite–Fe_2O_3	25–35
Al_2O_3	Diaspore–AlO(OH) Gibbsite–$Al(OH)_3$ Bayerit–$Al(OH)_3$ Sodalite–$Na_4Al_3Si_3O_{12}Cl$	22–28
SiO_2	Quartz–SiO_2 Sodalite–$Na_4Al_3Si_3O_{12}Cl$	6–16
Na_2O	Sodalite–$Na_4Al_3Si_3O_{12}Cl$	4–9
$CaO + MgO$	–	0.5–4
TiO_2	Anatase–TiO_2	8–24
LOI	$H_2O + CO_2$	7–12

LOI: loss on ignition.

Result and discussions

As part of our research on chemical transformations (*30*), in this paper we report a green, simple and environmentally benign methodology for the synthesis of olefinic compounds via Knoevenagel condensation using RM as the catalyst.

The RM catalyzed Knoevenagel reaction was first studied using benzaldehyde and ethyl cyanoacetate in ethyl acetate as a solvent at room temperature. The Knoevenagel adduct was isolated in high yield. In this experiment, the product was isolated by filtration, the solid residue was washed with ethyl acetate, and the remaining RM reloaded with fresh reagents for further runs. No considerable decrease in the yield was observed, demonstrating that RM can be reused as a catalyst in Knoevenagel condensations. The results encouraged us to work on the Knoevenagel condensation using a column packed with powdered RM. Reactants were added to the top of the column and eluted using ethyl acetate. The mixture was collected, the solvent was evaporated, and products were obtained in excellent yields. To examine the reusability of this column for Knoevenagel condensations, the above process was repeated three times for condensation of benzaldehyde with ethyl cyanoacetate. The second and third runs, according to this procedure, showed no considerable decrease in the reaction yield.



Scheme 1.

The greenness of a process is determined by many factors and E-factor is an important one that is defined as (*31*):

$$\text{E-factor} = \text{total waste (kg)/product (kg)}$$

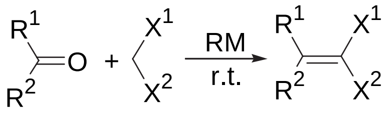
In this work, the E-factor of a column packed system is lower than a heterogeneous system. Therefore, the column packed system is better than the heterogeneous system using this metric.

These results encouraged us to develop a column packed system for the condensation of a broad spectrum of aromatic and heteroaromatic aldehydes with active methylene compounds, as shown in Scheme 1. The results are summarized in Table 2.

The Knoevenagel condensation of aliphatic aldehydes and ketones with active methylene compounds were also investigated and Scheme 2 and Table 3 clearly show the results.

Table 2. Condensation of active methylene compounds with aromatic aldehydes.

Entry	Ar	X^1	X^2	Yield (%)	Mp (°C) (found)	Mp (°C) (reported)
1	C_6H_5	CN	CN	95	84–85	83 (*32*)
2	4-Me_2N-C_6H_4	CN	CN	86	160	160 (*33*)
3	4-NO_2-C_6H_4	CN	CN	97	160	160 (*34*)
4	2-Cl-C_6H_4	CN	CN	94	92–94	93 (*34*)
5	$C_6H_5CH{=}CH$	CN	CN	93	126	128 (*35*)
6	3-NO_2-C_6H_4	CN	COOMe	90	135	135 (*36*)
7	4-Cl-C_6H_4	CN	COOEt	98	91–92	91 (*33*)
8	4-OH-C_6H_4	CN	COOEt	86	136–137	135 (*37*)
9	2-Furyl	CN	COOEt	96	91–93	91–93 (*38*)
10	4-Me_2N-C_6H_4	CN	COOEt	92	125	125 (*36*)
11	4-NO_2-C_6H_4	CN	COOEt	97	168	170 (*39*)
12	3-Cl-C_6H_4	CN	COOEt	95	100–101	101–102 (*40*)
13	3-NO_2-C_6H_4	CN	COOEt	89	139	139 (*34*)
14	$C_6H_5CH{=}CH$	CN	COOEt	91	114–115	115–116 (*41*)
15	4-MeO-C_6H_4	CN	COOEt	75	78–79	79–81 (*41*)
16	4-NO_2-C_6H_4	COOEt	COOEt	63	63	65 (*42*)



Scheme 2.

Table 3. Condensation of active methylene compounds with aliphatic aldehydes and ketones.

Entry	R^1	R^2	X^1	X^2	Yield (%)
1	Me	Me	CN	COOEt	81
2	Me	Et	CN	CN	85
3	Me	Ph	CN	COOEt	63
4	Me	H	CN	COOEt	71
5	Et	H	CN	CN	49

Experimental

General methods

Melting points were measured on an Electrothermal 9100 apparatus and were uncorrected. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 AVANCE spectrometer at 500.13 and 125.77 MHz, respectively. NMR spectra were obtained in solutions of $CDCl_3$. Chemical analysis of RM was determined with XRF (Bruker S4 EXPLORER). The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and Merck Chemical Company. The RM used in this work was obtained from Indian Gibbsite Bauxite. The composition of the RM sample was obtained by X-ray fluorescence (XRF) and is shown in Table 4.

Column preparation

The RM was ground in a mortar to particle sizes between 40 and 60 mesh (250–350 μm) and packed in a column (1 cm diameter and 10 cm length).

General procedure

Benzaldehyde (5 mmol) and ethyl cyanoacetate (5 mmol) were dissolved in ethyl acetate (2 ml), added to the top of the column, and eluted using ethyl acetate (15 ml). The mixture was collected at the bottom of the column; the solvent was evaporated and products were obtained in 98% yields. Further purification for some products was required and achieved by recrystallization from ethanol.

Conclusion

In conclusion, we have developed a new, simple and green method for Knoevenagel condensations using RM as the catalyst. The best achievements of our work were the use of one packed column for Knoevenagel reactions for a variety of aldehydes with active methylene compounds, and using a waste product of a Bayer process as the eco-friendly catalyst. In addition, in this process the catalyst separation step was eliminated from the reaction mixture.

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Table 4. XRF analysis of used RM.

Contaminates	Fe_2O_3	Al_2O_3	SiO_2	Na_2O	TiO_2	CaO	ZrO_2
Content (w%)	25.13	19.51	18.5	11.04	3.79	3.06	0.45
Contaminates	K_2O	MgO	MnO	SO_3	Cl	P_2O_5	LOI
Content (w%)	0.39	0.22	0.07	1.23	0.33	0.27	16.01

LOI: loss on ignition.

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