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# Molybdenum carbide as an efficient and durable catalyst for aqueous Knoevenagel condensation<sup>†</sup>

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By following green chemistry principles, various molybdenum compounds as cost-effective, commercially available, heterogeneous, and benign catalysts were used for the Knoevenagel condensation reaction. Among the compounds (Mo<sub>2</sub>C, MoS<sub>2</sub>, MoB, MoSi<sub>2</sub>), molybdenum carbide showed efficient performance for the Knoevenagel condensation in aqueous media at room temperature, affording the corresponding products in high yields within a short reaction time. Notably, using this commercially available heterogeneous catalyst, the deacetalization-Knoevenagel condensation of benzaldehyde dimethyl acetal and malononitrile at room temperature could successfully proceed in excellent yield. Molybdenum carbide could be recovered five times without loss of activity with an operationally simple procedure.

### Introduction

Catalysts, as the heart of chemical reactions, play a critical and key role in chemical processes in both academic and industrial research labs. For this reason, many attempts have been devoted to the use of simple, efficient, economic, and eco-friendly catalysts which are easily prepared and can be extracted from the reaction mixture without tedious steps.

In recent years, molybdenum compounds have attracted significant attention as earth-abundant, inexpensive, and benign catalysts.<sup>1–3</sup> Particularly, molybdenum carbides have been successfully used in various reactions such as desulfurization,<sup>4,5</sup> water–gas shift,<sup>6</sup> and hydrogenation reactions.<sup>7,8</sup> It was found, by using experimental and theoretical studies, that transition metal carbides

(TMCs) have higher activity and durability compared to their parent metals and could show a behavior similar to noble metals in surface catalysis. These unique properties arise from the addition of carbon that causes an alteration in the electronic properties of these materials.<sup>9</sup>

The Knoevenagel reaction is a powerful synthetic method for the formation of the C—C bond.<sup>10,11</sup> The valuable  $\alpha$ , $\beta$ -unsaturated products obtained by this transformation are important intermediates in the synthesis of natural products,<sup>12</sup> therapeutic agents,<sup>13</sup> polymers with different functional groups,<sup>14</sup> cosmetics, and perfumes.<sup>15</sup> Although this reaction seems to be convenient and simple, the disadvantages of applied catalytic systems including using expensive metal-based catalysts, tedious steps for the preparation of heterogeneous catalysts, high temperature, and performing in non-green solvent cause it to still be a matter of interest to chemists.<sup>16-19</sup>

Herein, we studied the efficiency of various molybdenum compounds as inexpensive and commercially available catalysts to perform the Knoevenagel condensation and one-pot deacetalization-Knoevenagel condensation of benzaldehyde dimethyl acetal in water as a green solvent at room temperature.

Firstly, to obtain the best reaction conditions, the reaction of benzaldehyde with malononitrile was chosen as the model reaction, the results are summarized in Table 1. Initially studies revealed that among the various applied molybdenum compounds (Mo<sub>2</sub>C, MoS<sub>2</sub>, MoB, MoSi<sub>2</sub>) used as the catalysts, molybdenum carbide was the best choice, affording the corresponding Knoevenagel adduct in 97% yield in water at room temperature (Table 1, entry 1).

These results for the model reaction were in agreement with the high ability of molybdenum carbide catalysts related to their unique d-band electronic structures, similar to group 8 metals (Pt, Pd, Rh, *etc.*).<sup>9</sup>

From Table 1, we found that the nature of the solvents had a great effect on the reaction yield. In this way, polar solvents such as  $H_2O$  and EtOH could afford the desired product in high yields, but in toluene and *n*-hexane as the representatives of non-polar solvents no promising results were obtained within



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Table 1 Optimization of the reaction conditions for the Knoevenagel condensation of benzaldehyde and malononitrile<sup>a</sup>



 $^a$  Reaction conditions: benzaldehyde (1 mmol), malononitrile (1.1 mmol), and 2.5 mL H<sub>2</sub>O, GC yields.  $^b$  10 mol% (20 mg) of the catalyst was used.  $^c$  2.5 mol% (5 mg) of the catalyst was used.

12 h (Table 1, entries 5–8). In addition, the reaction could not successfully proceed in the absence of solvent (Table 1, entry 9). Further studies revealed that increasing the loading of catalyst from 5 mol% to 10 mol% had no positive effect on the yield and time of the reaction (Table 1, entry 10). Also, decreasing the amount of the catalyst to 2.5 mol% caused a great drop in the yield, 53% in 2 h (Table 1, entry 11).

With the optimal reaction conditions in hand (Table 1, entry 1), we then explored the substrate scope of the reaction for other aldehydes (Table 2). Aromatic aldehydes bearing either electrondonating or electron-withdrawing substituents in the para, meta and ortho positions furnished the corresponding Knoevenagel products in high yields (Table 2, 3a-h), without being affected by the electronic effect of the substituent. Interestingly, a 97% yield was obtained even for the challenging 2,4-Me-benzaldehyde that suffers from steric hindrance (Table 2, 3b). Notably, our procedure was efficient in the case of 1-naphthaldehyde and E-cinnamaldehyde as well as a heteroaryl aldehyde like 2-thiophenecarboxaldehydeand 3-pyridinecarboxaldehyde (Table 1, 3i-l). Also, the aliphatic aldehydes that are classified as challenging precursors showed good results as can be seen in Table 2, 3m, albeit with longer reaction times than the aromatic aldehydes (3h). Furthermore, the reaction was also performed with ketones, namely, cyclohexanone and 4nitro-benzophenone (Table 1, 3n-o), which resulted in a very good yield of the products with a longer reaction time than the aldehydes, indicating the high efficiency of molybdenum carbide as a catalyst for Knoevenagel condensation reactions.

Encouraged by these results, we turned our efforts toward using this catalyst to the one-pot deacetalization-Knoevenagel reaction of benzaldehyde dimethyl acetal. Surprisingly, 5 mol% of Mo<sub>2</sub>C could successfully furnish the corresponding Knoevenagel product in high yield at room temperature in 6 h (Scheme 1). As shown in Table 3, this catalytic activity compared to other reports which used synthesized heterogeneous catalysts is very impressive.

Table 2 Scope of the Knoevenagel condensation reaction by  ${\sf Mo}_2{\sf C}$  at room temperature<sup>a</sup>



 $^a$  Reaction conditions: benzaldehyde (1 mmol), malononitrile (1.1 mmol), Mo<sub>2</sub>C (5 mol%, 10 mg) and 2.5 mL H<sub>2</sub>O, GC yields.



Scheme 1 Deacetalization-Knoevenagel reaction of benzaldehyde dimethyl acetal using molybdenum carbide.

Notably, most of the previous systems employed organic solvents and the reaction was performed at high temperature to achieve satisfactory results (Table 3). However, we used a green route with much lower amounts of catalyst (10 mg) at room temperature in water.

In the next part of this study, we examined the reusability of this commercially available catalyst in the model reaction between benzaldehyde and malononitrile under optimized reaction conditions (Table 1, entry 1). When the first run of the reaction was completed, ethyl acetate was added to the reaction mixture and owing to the good dispersion of  $Mo_2C$  in water, the product and unreacted substrates were successfully extracted. Then, for the next run, only substrates were added to the aqueous phase containing the catalyst. Using this simple recycling method, the catalyst could be recovered five times while maintaining high activity (Fig. 1).

Table 3 Comparing the catalytic activity of the present system with previous catalysts in the one-pot deacetalization-Knoevenagel reaction of benzaldehyde dimethyl acetal (1 mmol) and malononitrile

Entry	Catalyst (mol%)	Conditions	Yield (%)	Ref.
1	MIL-101 MOFs (0.04 mmol)	DMF, 2 h, 90 °C	99	20
2	Ln cluster-based MOFs (100 mg)	DMSO-d <sub>6</sub> , 24 h, 50 °C	97	21
3	OMCN-1 (60 mg)	Toluene, 24 h, 80 °C	99	22
4	MOF (JUC-199) (100 mg)	1,4-Dioxane, 4 h, 90 °C	99	23
5	PCN-222-Co@TpPa-1 (50 mg)	DMSO-d <sub>6</sub> , 10 h, 50 °C	99	24
6	BNP (40 mg)	Toluene, 24 h, 80 °C	99	25
7	SO <sub>3</sub> H-AA@MNP (10 mg)	Toluene, H <sub>2</sub> O (11 mmol), 2 h, 90 $^\circ$ C	94	26







Scheme 2 Suggested mechanism for the Knoevenagel reaction catalyzed by  $Mo_2C$ .

Next, the XRD pattern of the  $Mo_2C$  catalyst after six runs in the reaction was recorded and compared with that of the fresh catalyst, Fig. 2. Both XRD patterns revealed that Mo had not changed during the reaction, so losing some of the catalyst during the recovery process could probably be considered responsible for the deactivation observed.<sup>27</sup>

However, the proposed mechanism for the role of the catalyst is shown in Scheme 2. Generally, the reactant molecules were attached to the Mo<sub>2</sub>C surface, and a C–C bond was formed due to the bifunctional properties of the catalyst.<sup>28</sup> Simultaneously, polar solvents such as water bonded to nearby Mo atoms and accelerated the formation of the product.

In summary, we used molybdenum carbide as a recyclable and commercially available catalyst for the Knoevenagel condensation reaction. The reaction performed well over a range of aldehydes, especially aliphatic and heteroaromatic aldehydes, giving the corresponding products with up to 95% yield. Also, cyclohexanone and 4-nitro-benzophenone as representatives of ketones, gave the desired products in high yields. Particularly, using this catalytic system, the one-pot deacetalization-Knoevenagel



Fig. 2 XRD patterns of fresh and reused Mo<sub>2</sub>C.

reaction of benzaldehyde dimethyl acetal proceeded very well with similar conditions and yields to the benzaldehyde substrate albeit with longer reaction time. The catalyst could be recycled five times without significant loss of catalytic activity. Thus, this commercially available and recoverable catalyst can be considered as a promising catalytic system, especially in industrial applications.

## Experimental

#### **General information**

Reagents obtained from commercial sources were used without further purification. Molybdenum compounds and malononitrile were purchased from Aldrich Company. Gas chromatography analyses were obtained on a Varian CP-3800 using a flame ionization detector (FID). <sup>1</sup>H-NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl<sub>3</sub>:  $\delta$  = 7.29). <sup>13</sup>C-NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling.

# General procedure for the Knoevenagel condensation reaction using Mo<sub>2</sub>C catalyst

A 5 mL round-bottomed flask was charged with a carbonyl compound (1 mmol), malononitrile (1.1 mmol), Mo<sub>2</sub>C (10 mg) and H<sub>2</sub>O mixture (2.5 mL). Then it was stirred at room temperature under argon atmosphere. After completion of the reaction (monitored by GC), the mixture was extracted by ethyl acetate ( $2 \times 5$  mL). The organic phase was dried with anhydrous

 $Na_2SO_4$ , and then evaporated under reduced pressure. The pure products were obtained after recrystallization in ethanol.

# Conflicts of interest

There are no conflicts to declare.

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