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Supported organic catalysts: synthesis of (*E*)-nitrostyrenes from nitroalkanes and aromatic aldehydes over propylamine supported on MCM-41 silica as a reusable catalyst

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Abstract—MCM-41-supported propylamine showed high catalytic efficiency in the nitroaldol condensation between nitroalkanes and aromatic aldehydes. © 2001 Elsevier Science Ltd. All rights reserved.

Mesoporous MCM-type silicas represent ideal inorganic supports for immobilised catalysts due to their high surface area and sharply distributed pore dimensions in the mesoporous range[1] that allow easy access to the reagents.[2] Organic bases can be anchored to these materials using the post-modification methodology[3] or, directly, by co-condensation of conveniently functionalised siliceous precursors.[4]

In connection with our interest in the preparation and use of solid catalysts for the production of fine chemicals,[5] we report here the results of a study on the catalytic efficiency of aliphatic amines supported on MCM-41 silica[6] for the nitroaldol condensation between nitroalkanes and aromatic aldehydes to give (*E*)-nitrostyrenes.

Nitroaldol condensation is routinely performed in the presence of a wide range of base catalysts. Nitroalcohols firstly produced can undergo water elimination to give nitroalkenes. The intermediacy of imines in the reaction promoted by primary amines was postulated even if studies in this area are quite contradictory.[7]

The functional aminopropyl groups were anchored on MCM-41 silica by the post-modification method[3] using 3-aminopropyltriethoxysilane, *N*-methyl-3-aminopropyltrimethoxysilane and *N*,*N*-diethyl-3-aminopropyltrimethoxysilane to give solid basic catalysts called MCM-41-NH_2, MCM-41-NHMe and MCM-41-NEt_2, respectively.

All supported catalysts (50 mg) were tested in the model reaction of benzaldehyde (2.5 mmol) with nitromethane as the solvent reagent (3 ml). Yields and selectivities of the corresponding product **3** for all experiments are reported in Table 1. For comparison, the reaction was carried out over unfunctionalised MCM-41 silica.

The inert nature of the amine-free material (entry a) suggests that the supported amines are responsible for the activity and whose efficiency follows the trend primary$\gg$secondary>tertiary (entries b–d), in disagreement with the tabulated basicity order of aliphatic amines in polar solvents.[8]

These features, along with the reported remarkable ease with which aromatic aldehydes give rise to the supported imines by reaction with aminopropylsilica,[9] allow us to formulate the mechanistic hypothesis depicted in Scheme 1.

The primary step is the condensation of the supported propylamine **4** with benzaldehyde, which affords the supported imine **5**. Addition of nitromethane (activated as a nitronate anion) to the carbon–nitrogen double bond via a nitro-Mannich process,[10] would give the relatively unstable supported β-nitroamine **6**.[11] The final step is β-scission of **6** that produces nitrostyrene **3** and regenerates the catalyst **4**, closing the cycle.[12]

Keywords: aldol reaction; catalysts; imines; nitrocompounds.

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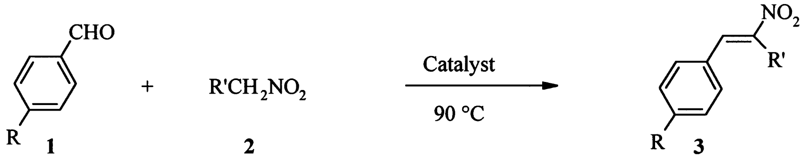
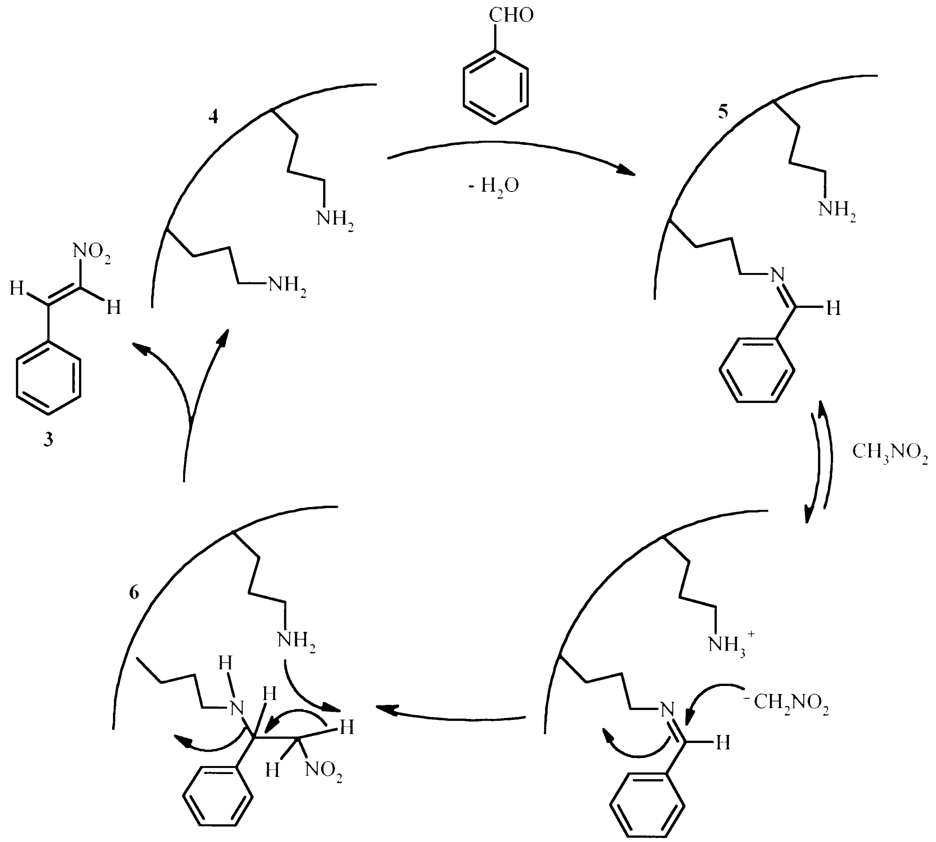
Table 1. Condensation between nitroalkanes and aromatic aldehydes under different conditions



Entry	Catalyst	R	R′	Time (h)	**3** Yield (%)	**3** Selectivity (%)
a	MCM-41	H	H	1	–	–
b	MCM-41-NEt$_2$[a]	H	H	1	5	99
c	MCM-41-NHMe[a]	H	H	1	34	81[b]
d	MCM-41-NH$_2$[a]	H	H	1	98	99
e	MCM-41-NH$_2$[a]	Me	H	1	97	98
f	MCM-41-NH$_2$[a]	OMe	H	1	96	99
g	MCM-41-NH$_2$[a]	NO$_2$	H	1	98	99
h	MCM-41-NH$_2$[a]	Cl	H	1	97	98
i	MCM-41-NH$_2$[a]	H	Me	6	95	97
j	MCM-41-NH$_2$[a]	OMe	Me	6	95	98
k	MCM-41-NH$_2$[a]	Cl	Me	6	98	99
l	MCM-41-NH$_2$[a]	Cl	Et	6	88	98
m	MCM-41-NH$_2$[a]	NO$_2$	Et	6	92	97

[a] The loading of MCM-41-NEt$_2$, MCM-41-NHMe and MCM-41-NH$_2$ was 1.23, 1.33 and 1.36 mmol *N* g^{-1}, respectively.

[b] 1,3-Dinitro-2-phenylpropane was isolated as a by-product.



Scheme 1. A hypothesised catalytic cycle of the MCM-41-NH$_2$-promoted nitroaldol condensation.

In order to support the mechanistic hypothesis depicted in Scheme 1 and to find out any transformation of the catalyst occurring during the reaction, FT-IR spectra of the catalyst (MCM-41-NH$_2$) before and after treatment with benzaldehyde were compared. The appearance of a new peak at 1646 cm^{-1} (C=N),[13] in addition to the two peaks at 3357 and 3280 cm^{-1} (NH$_2$) in the benzaldehyde-treated catalyst **5**, suggests the co-existence of both supported propylamine and benzylidene propylamine. The FT-IR spectrum of material **5** after further treatment with nitromethane at 90°C for 1 h was quite similar to that of the starting MCM-41-NH_2. At the same time, nitrostyrene was detected in the solution by GC analysis. These data support the mechanism reported in Scheme 1 but, at the same time, do not exclude the co-existence of the classical one.[7b]

Repeated condensation tests were successively performed for five cycles under the above-reported conditions. The catalyst was removed after each cycle, washed with nitromethane and reintroduced into the reactor; a new batch of benzaldehyde and nitromethane was then added and the reaction was repeated under the same conditions. Compound **3** was detected in 98, 95, 95, 90 and 84% yield. These results show that the catalyst MCM-41-NH_2 was reusable for all the five cycles, showing only a small lowering of the conversion in the fourth and fifth cycles.

The reaction has been successfully extended to different aromatic aldehydes and nitroalkanes giving products **3** in high yield and excellent selectivity.[14] In all cases, the (*E*)-stereoisomer was the sole product detected (Table 1, entries e–m).[15]

In summary, in the present paper we have shown that aminopropyl silica acts as a heterogeneous organic catalyst in the nitroaldol condensation between aromatic aldehydes and nitroalkanes. The results suggest that the supported primary aminopropyl moiety reacts with the aldehyde giving an imine intermediate, which in turn undergoes nitro-Michael attack producing nitrostyrene as the final product through the unstable supported nitroamine intermediate **6**.

In addition, the use of a supported catalyst that can be easily removed from the reaction mixture by filtration has the great advantage of avoiding base-catalysed by-product formation during the work-up procedure.[7b]

Acknowledgements

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