High Surface Area MgO as a Highly Effective Heterogeneous Base Catalyst for Michael Addition and Knoevenagel Condensation Reactions

Chunli Xu, Jonathan K. Bartley, Dan I. Enache, David W. Knight, Graham J. Hutchings*

Cardiff University, School of Chemistry, Main Building, Park Place, Cardiff, CF10 3AT, UK
Fax +44(29)20874075; E-mail: hutch@cf.ac.uk

Received 22 September 2005

Abstract: Magnesium oxide (MgO), obtained using a novel but simple procedure, was systematically investigated as a heterogeneous base catalyst for reactions taking place in the liquid phase, specifically the Michael addition and the Knoevenagel condensation. The activity of MgO was studied in detail, together with the effects of solvent and substrate on the catalytic activity for each type of reaction. A key finding is that the formation of enols affected the activity of MgO. The experimental results show that the activity of MgO did not change when it was reused and it is an excellent heterogeneous catalyst for the reactions studied.

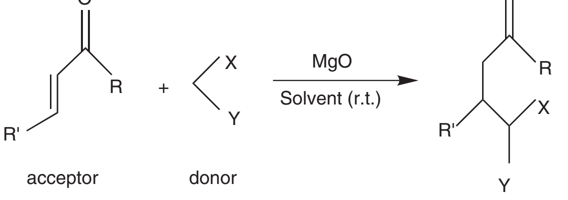
Key words: Michael addition, Knoevenagel condensation, solvent effect, enol effect, basic catalysis

In recent years, there has been increasing emphasis on the design and use of environmentally friendly solid acid and base catalysts to reduce the amount of toxic waste and byproducts arising from chemical processes prompted by stringent environment protection laws.[1] In contrast to the extensive studies involving heterogeneous acid catalysts, fewer efforts have been made to develop heterogeneous base catalysts.[2,3] Several solid bases have been reported as being effective in this respect: (1) zeolites such as alkali ion-exchanged zeolites[4,5] and sodium metal clusters in zeolites;[6] (2) supported alkali metal ions including alkaline oxides supported on microporous[7] and mesoporous solids,[8] alkali metals supported on alumina (Na/NaOH/γ-Al_2O_3);[9] (3) clay minerals, for example sepiolites[10] and hydrotalcites (HDT);[11–13] (4) non-oxide bases including phosphates[14–17] and nitrides;[18,19] (5) single-component catalysts such as alkaline earth solids;[20,21] and (6) mixed metal oxides, for example magnesium–lanthanum mixed oxide.[22]

Amongst these solid bases, hydrotalcite (HDT) or hydrotalcite-like compounds have recently been studied the most. The basic properties of HDT can be modified by rehydration or ion exchange, which improves the activity of these catalysts.[1,23–25] For example, HDT can be modified by anion exchange with KF to obtain HDT-F.[24] However, this process is complex, costly, and requires experienced people to operate it. As the cost of fabricating a catalyst can be a critical factor in its industrial applications, few commercial materials have been synthesized in this way. In contrast, MgO is inexpensive and easily obtained. This attracted us to explore the possibility of preparing more active versions, which could find applications in large-scale manufacture. It is a mild base and has the lowest solubility among the alkaline earth oxides and so can potentially be reused as it will not be lost due to leaching into the reaction mixture. However, the applications of MgO as a basic catalyst in liquid reactions have been very limited because MgO showed low activity in the reactions tested.[26] We have found that MgO with a high surface area can be produced, and in this study, we have systematically investigated MgO as a solid base catalyst for Michael additions and Knoevenagel condensations, reactions which are commonly used in the manufacture of fine chemicals.

The particular versions of the Michael addition studied were the addition of active methylene compounds, alcohols, and thiols to α,β-unsaturated carbonyl compounds, a useful strategy for the construction of carbon–carbon bonds (Scheme 1). The mechanism for such Michael additions involves the formation of an anion from the active methylene compound, conjugate addition of this to the α,β-unsaturated carbonyl compound, and finally product protonation.[2] The Knoevenagel condensation (Scheme 2) of active methylene compounds and aldehydes is one of the most popular methods of synthesizing functionalized alkenes. Basic catalysts can generate significant amounts of carbanions from active methylene compounds, which can then attack a carbonyl group to give the condensation product.[27]

Base-catalyzed Michael additions and Knoevenagel condensations have been extensively studied in homogeneous systems,[28,29] but very few studies have employed hetero-



Scheme 1

Scheme 2

SYNTHESIS 2005, No. 19, pp 3468–3476
Advanced online publication: 14.11.2005
DOI: 10.1055/s-2005-918467; Art ID: C08805SS

geneous catalysts.[1] To date the heterogeneous catalysts studied have shown either low activity or have been prepared in a complex way.[23,30] To the best of our knowledge, there are no reported studies systematically dealing with the activity of MgO in such Michael additions, in particular, the catalyst preparation method, reaction conditions, and most importantly, the interaction between MgO and the substrate. In homogeneous base-catalyzed systems, the reaction rate increases with the pKa value (acid value) of the substrate and the basic strength of the catalyst. In the heterogeneous base-catalyzed system, there have been no studies which systematically investigate the relationship between the acid value of the substrate and the activity of MgO. This will be critical for preparing a successful solid basic catalyst.

In this paper we investigate a high area form of MgO as a catalyst for a number of different Michael additions and Knoevenagel condensations and it was found to be very active and reusable. It was also found that the activity of MgO, to a large extent, depended upon the solvent and the structure of the substrate. The effect of substrate acidity in the heterogeneous system with MgO is different from homogeneous base-catalyzed systems. This discovery may be very helpful for future studies of other metal oxide catalysts. Finally, we propose mechanisms for these reactions involving MgO catalysis.

Michael Addition Reaction

Figure 1 presents the variation of the conversion of chalcone and diethyl malonate after a reaction time of 30 minutes as a function of the calcination temperature. Calcination of the catalyst below 400 °C, leads to a very low conversion. A calcination temperature of 400–500 °C gave maximum conversion. When the catalyst was calcined above 500 °C, the activity of MgO decreased and continued to decrease as the calcination temperature increased. The results are consistent with changes in the surface area of the catalyst, which varies with calcination temperature (Figure 1), the maximum surface area was obtained after calcining the samples at 400–500 °C.

The XRD pattern of the precursors did not change when the calcination temperature was below 400 °C (Figure 2), however, MgO was only observed when the calcination temperature was higher than 400 °C. As the calcination temperature was increased to 600 °C, MgO became more crystalline resulting in a loss of surface area.

Results of the Michael addition reactions are presented in Table 1. The conversion was calculated by the decrease in the amount of the α,β-unsaturated carbonyl compound. MgO was found to be an efficient and selective catalyst for 1,4-addition to chalcone. MgO was found to be more active compared with other catalysts reported in the literature such as HDT-F, HDT-*t*-BuO, HDT-OH, $Ba(OH)_2$, and xonotlite and it was prepared using a much simpler procedure.

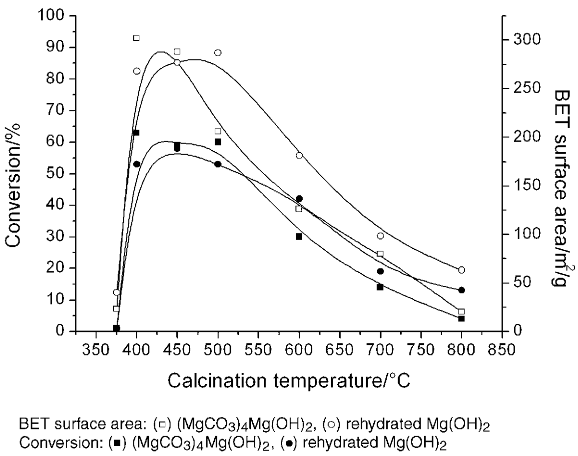


Figure 1 The effect of calcination temperature on the activity of MgO for the Michael addition between chalcone and diethyl malonate.

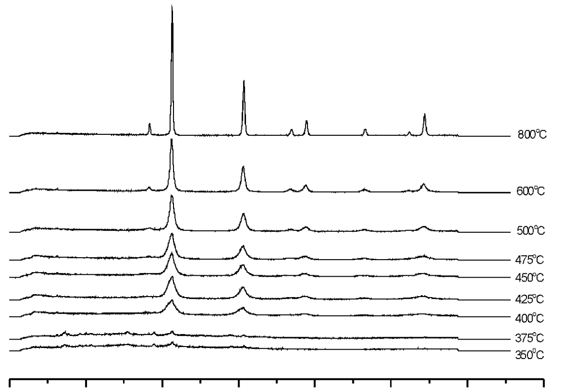


Figure 2 The powder X-ray diffraction patterns of MgO calcined at different temperatures.

The activity of the catalyst was obtained for a number of different donor species (Table 2). The results show that the Michael additions were not affected by the pKa value of the nucleophile. Theoretically, the lower the pKa value of the donor, the easier to abstract the proton and, therefore, form the carbanion and perhaps the Michael adduct. Several structurally diverse nucleophiles such as malononitrile (Table 2, entry 6, pKa 11.1), ethyl cyanoacetate (Table 2, entry 7, pKa 13.1), and diethyl malonate (Table 2, entry 8, pKa 16.4) underwent clean and remarkably fast Michael additions to chalcone by this procedure (Scheme 1). However, 2,4-pentanedione (Table 2, entry 2, pKa 13.3) and ethyl acetoacetate (Table 2, entry 4, pKa 14.3), which are more acidic than diethyl malonate did not undergo fast Michael addition. In the case of 2,4-pentanedione, no conversion was obtained after the reaction time was extended to 36 hours. This low activity can be ascribed to the formation of a *cis*-enol **2b** (Scheme 4).

Table 1 Michael Additions Catalyzed by MgO

Entry	Acceptor	Donor	Solvent	Time (h)	Yield (%)
1	Chalcone	Diethyl malonate	Toluene	2	93
				2[a]	95
				2[b]	95
				48[c]	75
				6[d]	96
				8[e]	95
2	Chalcone	Ethyl cyanoacetate	Toluene	0.5	88
				–[e]	Complex mixtures
3	2-Cyclohexen-1-one	Dimethyl malonate	Toluene	1	93
				1[b]	90
4	Methyl crotonate	*p*-Toluenethiol	Toluene	0.5	100
5	4-Phenyl-3-buten-2-one	Malononitrile	Toluene	1	13
6	Chalcone	Malononitrile	MeCN	1.5	88
				2[d]	88

[a] HDT-F.[24]
[b] HDT-*t*-BuO.[23]
[c] Using *t*-BuOK on xonotlite as catalyst.[30]
[d] HDT-OH.[31]
[e] $Ba(OH)_2 \cdot 1\text{–}1.5H_2O$.[32]

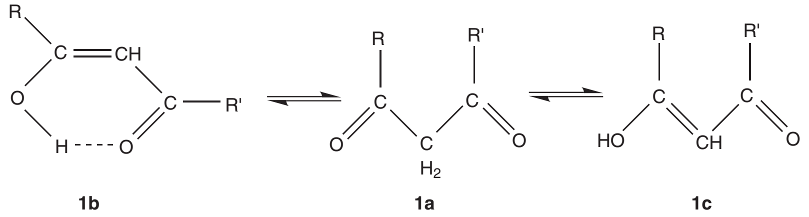
Table 2 Effect of the Donor Using Chalcone as the Acceptor

Entry	Donor	pKa in DMSO	Solvent	Time (h)[a]	Yield (%)[a]
1	*p*-Toluenethiol	10.3	Toluene	0.5	17
2	2,4-Pentanedione	13.3	Toluene	0.5 (36)	0 (0)
3	5,5-Dimethyl-1,3-cyclohexanedione (**3a**)	11.2	DMSO	0.5 (21)	7 (90)
4	Ethyl acetoacetate	14.3	Toluene	0.5 (21)	0 (7)
5	Nitromethane	17.2	Toluene	0.5	7
6	Malononitrile	11.1	MeCN	0.5	80
7	Ethyl cyanoacetate	13.1	Toluene	0.5	88
8	Diethyl malonate	16.4	Toluene	0.5	69

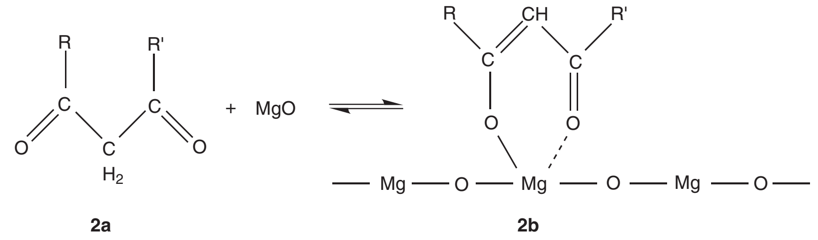
[a] The number in parenthesis corresponds to the extended reaction time and the yield observed.

In general, 1,3-dicarbonyl compounds, which include β-diketones and β-keto-esters, may exist in three tautomeric forms: the diketo form **1a**, the *cis*-enolic form **1b**, and the *trans*-enolic form **1c** (Scheme 3).[33] Open-chain 1,3-dicarbonyl compounds are rarely observed in the *trans*-enolic form. In solution, such compounds enolize practically exclusively to the *cis*-enolic form **1b**, which is stabilized by intramolecular hydrogen bonding.

When MgO was added to a solution of 2,4-pentanedione, the new *cis*-enol **2b**, which is stabilized by the intramolec-



Scheme 3



Scheme 4

ular Mg–O bond, was presumably formed (Scheme 4).[34] This *cis*-enol is so strongly adsorbed onto the catalyst surface that the active site is blocked and the activity stops. To confirm this, three reactions between diethyl malonate and chalcone were conducted as shown in Figure 3. For the reaction conducted without 2,4-pentanedione, the conversion increased steadily with time. However, when 2,4-pentanedione was added after running the reaction for ten minutes, the conversion stopped. Finally, if 2,4-pentanedione was added before the reaction began, the reaction rate decreased dramatically.

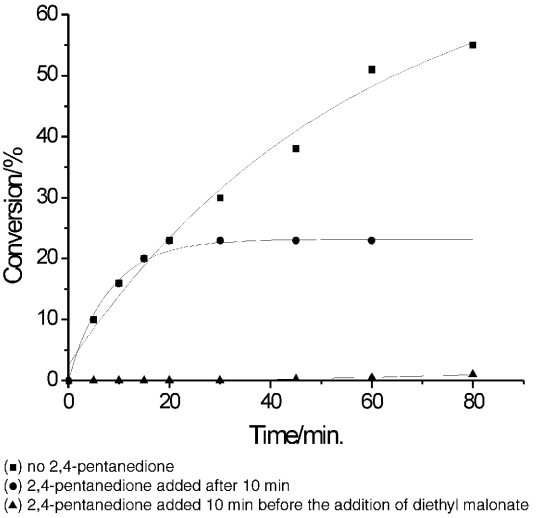
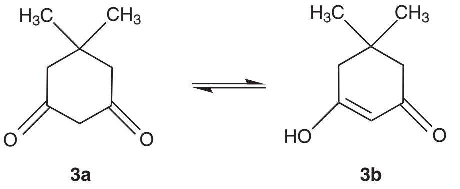


Figure 3 The effect of 2,4-pentanedione on the Michael addition between chalcone and diethyl malonate.

In contrast, cyclic 1,3-dicarbonyl compounds, e.g. 5,5-dimethyl-1,3-cyclohexanedione **3a** (Scheme 5), can only exist as a *trans*-enol **3b** (Scheme 5) and intramolecular hydrogen bonding is not possible. When MgO is added to a solution of 5,5-dimethyl-1,3-cyclohexanedione, the *cis*-enol with an intramolecular Mg–O bond is therefore impossible. As predicted, it was found that the product of the Michael addition with 5,5-dimethyl-1,3-cyclohexanedione (Table 2, entry 3) can be obtained with high conversion. The activity of nitromethane can be ascribed to the nitro/aci-nitro tautomerism[35] and low pKa value (Table 2, entry 5).



Scheme 5

When methyl crotonate was used as the acceptor, high conversion was obtained only with *p*-toluenethiol (Table 3). Compared with chalcone, the charge at the β-position of methyl crotonate is less positive. Since the same MgO catalyst and reaction conditions were used for these reactions, the proton-abstracting ability of MgO did not change. Therefore, it can be proposed that proton abstraction is not the crucial step, hence, the lower electrophilicity of the acceptor crotonate is probably the key factor preventing reaction.

Table 3 Effect of the Donor with Methyl Crotonate as the Acceptor[a]

Entry	Donor	pKa in DMSO	Time (h)	Yield (%)
1	*p*-Toluenethiol	10.3	0.5	44
2	2,4-Pentanedione	13.3	0.5	0
3	Ethyl acetoacetate	14.2	0.5	0
4	Nitromethane	17.2	0.5	0
5	Malononitrile	11.1	0.5	0
6	Ethyl cyanoacetate	13.1	0.5	0
7	Dimethyl malonate	16.4	0.5	0
8	MeOH	29	0.5	0

[a] Reactions were performed in toluene (10 mL).

One of the most important parameters for the success of the planned reaction is the selection of a suitable solvent (Table 4). When chloroform or methanol was used as the solvent, MgO was inactive but a high conversion could be obtained using hexane as the solvent. Chloroform is an aprotic and acidic solvent with high electrophilicity. It tends to coordinate strongly with anions, and consequently the attack of an anion onto α,β-unsaturated carbonyl compounds was blocked. Methanol is an acid and protic solvent, which stabilizes both anions and cations. Hexane is non-polar, essentially non-solvating, does not undergo auto-ionization, and plays a minimal role in the reaction.

Table 4 Solvent Effects on the Michael Addition[a]

Solvent	pKa	Polarity	Time (h)	Yield (%)
$CHCl_3$		4.1	2	–
MeOH	16	5.1	2	Trace
EtOAc	25	4.4	2	50
MeCN	25	5.8	2	50
Toluene	40	2.4	2	66
Hexane	48	0	2	80
DMSO	30	7.2	2	8

[a] Reagents and conditions: chalcone, diethyl malonate, solvent (10 mL).

Table 5 Reusability of MgO

Entry	Catalyst	S_{BET} (m^2/g)	Time (min)	Yield (%)
1	MgO (1st use)	288	30	54
2	MgO[a] (2nd use)		30	25
3	MgO[b] (2nd use)	239	30	34
4	MgO[c] (2nd use)	165	30	32
5	MgO[d] (2nd use)	287	30	50

[a] MgO was washed with toluene (3 ×); MgO was separated from toluene by centrifugation.

[b] MgO was washed with toluene before calcination.

[c] MgO was refluxed in toluene, filtered, washed with toluene, dried at 110 °C, and then refluxed in H_2O before calcination.

[d] MgO was washed with toluene, then refluxed in H_2O before calcination.

However, the solubility of the product in hexane is low, which may enhance the reaction rate.

Ethyl acetate, acetonitrile, and toluene are aprotic and basic solvents that tend to coordinate strongly with cations. This should result in the basicity of the solid base increasing. In the case of toluene, high conversions can be obtained and although the highest conversion was obtained with hexane, toluene was selected as the solvent for the Michael additions because of the toxicity of hexane.

In addition, the volume of the solvent used in the reaction affected the activity of MgO. For the Michael additions between chalcone and diethyl malonate it was found that with toluene as the solvent a higher concentration of reactants resulted in a higher conversion (1 mL per mmol of reactant, 93% conversion, 2 h; 5 mL per mmol of reactant, 66% conversion, 2 h), which may point to the reaction rate being influenced by the reactant concentration.

We also attempted to reuse the catalyst by a variety of methods (Table 5). Direct reuse of the catalyst (Table 5, entry 2) led to a greater than 50% decrease in activity while treatment of the catalyst prior to reuse also resulted in lower conversions (Table 5, entry 3,4). This phenomenon probably arose because the reactant and product were not completely desorbed from MgO and therefore, the active sites were blocked. However, we found that by washing MgO with toluene and then refluxing in water before calcinations, the catalyst could be recovered and reactivated (Table 5, entry 5). The activity and surface area for the freshly prepared and the reused catalyst are almost the same. It should be noted that the catalytic activity also decreased when the calcined catalyst was allowed to stand in air for a few hours before use, but such a loss of activity was not observed when the catalyst was stored in a desiccator over molecular sieves for one month.

In order to study the effect of water in the solvent, three reactions were carried out. One reaction was carried out in an anhydrous solvent (MeCN) and the other two in a solvent containing 2% water and 2% heavy water. Figure 4 shows the effect the presence of both water and heavy water had on the reaction causing the rate to decrease initially; however, neither influenced the overall yield of the reaction. Considering that the content of water in common solvents is less than 0.3%, for these reactions with MgO as catalyst, solvents can be used directly without drying.

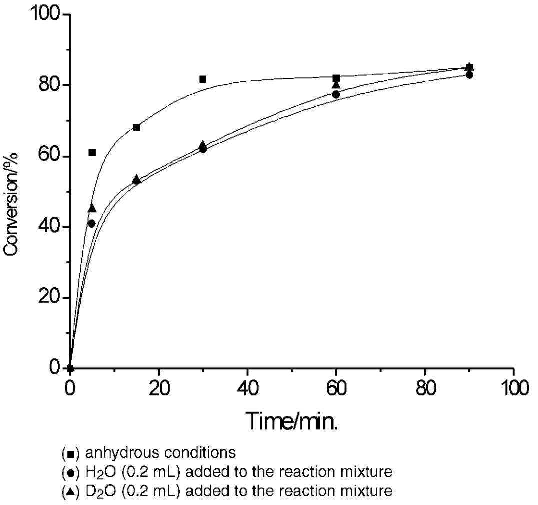


Figure 4 The effect of H_2O on the reaction between chalcone and malononitrile.

Both NMR spectroscopy and MS showed that D_2O did not undergo proton exchange with malononitrile, but did with the reactant chalcone and product. Therefore, it can be deduced that the Michael addition is an irreversible process, otherwise some of the malononitrile protons would have exchanged with the deuterium from D_2O.

Knoevenagel Condensation

Knoevenagel condensations involving aromatic carbonyl compounds with (a) malononitrile and (b) ethyl cyanoacetate (Scheme 2) as the active methylene compound were carried out at room temperature with MgO as catalyst and the results are reported in Table 6. The aromatic aldehydes readily condensed with malononitrile, while with

Table 6 Knoevenagel Condensation of Aldehydes with Ethyl Cyanoacetate and Malononitrile

Entry	R	R′	Solvent	Time (min)	Conversion (%)	Selectivity (%)
1	Phenyl	CN	DMF	5 30	94 100	100
2	Phenyl	CO_2Et	DMF	30	97	100
3	2-Furyl	CN	DMF	30	100	100
4	2-Furyl	CO_2Et	DMF	30	99.9	100
5	2-Methyl-butyl	CN	DMF	60	99	100
6	2-Methyl-butyl	CO_2Et	DMF	60	80	100
7	Butyl	CN	DMF	30	88	100
8	Butyl	CO_2Et	DMF	30	76	100
9	c-C_5H_{10}	CN	DMF	60	97	100
10	c-C_5H_{10}	CO_2Et	DMF	60	23	100
11	Cinnamyl	CN	DMF			
12	Cinnamyl	CO_2Et	DMF	60	50	57

ethyl cyanoacetate the reaction was slightly slower. This may be attributed to the fact that abstraction of a proton from the active methylene group of ethyl cyanoacetate was relatively more difficult due to its lower acidity. As can be seen from Table 6, all reactions proceeded selectively to the dehydrated products without any side reactions. The rate of reaction is high and was generally equal or better than those reported in the literature (Table 7).

An attempt was made to check the reusability of the catalyst in the following manner. The reaction was performed as usual for 30 minutes, then the stirring was stopped, and the reaction mixture was placed in a centrifuge for ten minutes. After the supernatant was separated from the catalyst, DMF was added and the mixture stirred, centrifuged, and separated a second time. Fresh reactants and solvent were added to the residual catalyst and the reaction was performed under identical conditions as before. As can be seen in Table 8, the activity and selectivity of the catalyst was found to be almost the same. The washing and relocation may result in some loss of catalyst, which probably explains why the conversion using the recovered MgO was slightly lower than in the case of fresh MgO.

Methanol is a good solvent for the reaction between benzaldehyde and malononitrile (Table 9, entry 1). However, there was no reaction using ethyl cyanoacetate in methanol; in contrast, DMF was found to be a good solvent with a high yield obtained after a reaction time of only 30 minutes.

Again, the volume of solvent used affected the activity of MgO. The concentration of the substrate was varied in both toluene (0.8 mL per mmol of reactant, 17% conversion, 30 min; 5 mL per mmol of reactant, 0% conversion, 30 min) and DMF; from these results we can conclude the higher the concentration of substrate the higher the reaction rate. It should also be noted that the Knoevenagel condensation product was formed with almost 100% selectivity in the presence of MgO, but in only 66% selectivity in the absence of MgO (Table 9, entry 2).

Of the seven substrates tested, only malononitrile and ethyl cyanoacetate resulted in high conversion (Table 10) while the other substrates gave rise to no Knoevenagel condensation product. The formation of enol forms can explain the lack of reactivity of 2,4-pentanedione and ethyl acetoacetate, whereas the activity of nitromethane can be ascribed to nitro/aci-nitro tautomerism[35] and its low pKa value.

The effect of the donor on the reaction may be used to determine the reaction mechanism. Scheme 6 has been proposed by Moison[20] as the mechanism for the Knoevenagel condensation. The mechanism for the Michael addition (Scheme 7) is based on the generally accepted route. Both of the intermediates (Schemes 6 and 7) can be confirmed by the effect the formed enols had on the reaction. The formation of the intermediate requires interaction between acid sites (Mg^{2+}) and acceptor, the conjugated basic sites and anion formed from methylene compounds. The formation of *cis*-enols between the open-chain 1,3-dicarbonyl compounds and the Mg^{2+} active site prevents the attack of the acceptor on the Mg^{2+} active site, and thus formation of the intermediate.

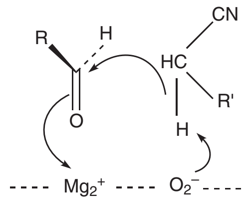
A simple method for the preparation of MgO, a catalyst that exhibits a high activity for base-catalyzed reactions, is described. The experimental results show that an optimal calcination temperature in the range 400–500 °C gives poorly crystalline, high surface area MgO that can be regenerated by washing, and then reused. The catalytic activity of such MgO for both Michael additions and Knoevenagel condensations was found to compare favorably

Table 7 Comparison of MgO with Different Heterogeneous Catalysts for the Knoevenagel Condensation between Benzaldehyde and Malononitrile

Catalyst	Catalyst amount	Reaction conditions	Time (min)	Conversion (%)	Yield (%)
MgO (this work)	**0.05 g**	**r.t., 2 mmol, MeOH (1.5 mL)**	**5** **30**	**94** **100**	
MgO[a,20]	4 g	r.t., 10 mmol	5		94
HDT[b,36]	5 wt%	60 °C	60	54	
MgO[b,36]	5 wt%	60 °C	60	62	
NiAlHTc[b,37]	0.05 g	60 °C, 1 mmol	30		97
HDT-OH[25]	0.05 g	r.t., 2 mmol, toluene (10 mL)	60		100
HDT-*t*-Bu[23]	0.05 g	r.t., 2 mmol, DMF (10 mL)	10		99
HDT-F[24]	0.035 g	r.t., 1 mmol, DMF (5 mL)	15		100
Zeolite[38]	50 wt%	r.t., 1:1.3, MeCN	720		78
Resin[39]	0.1 g	r.t., 10 mmol, benzene (5 mL)	300		92
KF/Al_2O_3[40]	0.78 g	r.t., 20 mmol, MeCN (15 mL)	150		80
FAP/BTEAC/water[b,41]	1.25 g	r.t., 1.5 mmol/2 mmol	4		98
$ZnCl_2$[b,42]	0.136 g	100 °C, 10 mmol	10		91
Aminosilica[43]	0.25 g	r.t., 20 mmol, solvent (25 mL)	240		99
$AlPO_4/Al_2O_3$ [b,44]	1.5 g	r.t., 10 mmol	15		80
$Na_2Ca_2P_2O_7$[17]	0.04 g	r.t., 1.5 mmol, MeOH (1.6 mL)	7		94
Xenotlite[b,30]	0.1 g	r.t., 10 mmol	1440		81

[a] Commercially available MgO.

[b] Reaction carried out in the absence of solvent.

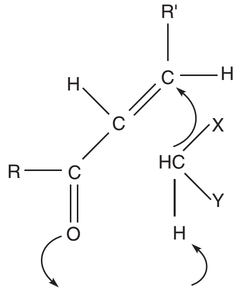


Scheme 6 Knoevenagel condensation

with previous studies using more complicated and expensive catalysts. Indeed, the simplicity of its preparation and the ease of reactivation after use may offer sufficient compensation to make MgO the base catalyst of choice even if slightly better yields can be obtained with alternative catalysts. It was found that the activity of MgO did not increase with the acidity of the substrate, in contrast to many homogeneous systems.

Table 8 Knoevenagel Condensation between Benzaldehyde and Ethyl Cyanoacetate with Fresh MgO and Reused MgO

Catalyst	Time (min)	Conversion (%)	Selectivity (%)
MgO (1st use)	30	94	100
MgO (2nd use)	30	90	100



Scheme 7 Michael addition

The catalysts used in this study were obtained by calcination of the precursors $(MgCO_3)_4Mg(OH)_2$, or rehydrated $Mg(OH)_2$ at 450 °C for 2 h. The heating ramp used in all cases was 10 °C/min. MS were carried on a Perkin-Elmer Turbomass GC-MS.

Table 9 The Effect of the Solvent on the Knoevenagel Condensation Reaction

Entry	R	R′	Solvent	Catalyst amount (g)	Time (min)	Conversion (%)	Selectivity (%)
1	Ph	CN	MeOH (1.6 mL)	0.05	30	100	100
2	Ph	CO_2Et	DMF (1.6 mL)	0.05	30	94	100
			DMF (5 mL)	0.05	30	77	100
				0	30	30	66
			DMF (10 mL)	0.05	30	69	100
			Toluene (1.6 mL)	0.05	30	17	100
				0.2	30	60	
			Toluene (10 mL)	0.05	30	0	
			MeOH (1.6 mL)	0.05	30	0	

Table 10 The Effect of the Donor on the Knoevenagel Condensation with Benzaldehyde

Entry	Donor	pKa in DMSO	Time (h)	Conversion/ %
1	2,4-Pentanedione	13.3	0.5	0
2	Ethyl acetoacetate	14.2	0.5	0
3	Nitromethane	17.2	0.5	0
4	Malononitrile	11.1	0.5	100
5	Ethyl cyanoacetate	13.1	0.5	97
6	Dimethyl malonate	16.4	0.5	0

Michael Addition

The reactions were carried out in a standard round-bottom glass flask equipped with a vertical condenser at r.t. under vigorous stirring. Reactions were performed with acceptor (2 mmol), donor (2 mmol), and catalyst (0.2 g), in toluene (2 mL) or MeCN (5 mL) at r.t. for the specified time.

Knoevenagel Condensation

Reactions were performed with acceptor (2 mmol) and donor (2 mmol) using MgO (0.05 g) in DMF (2 mL) or MeOH (5 mL) at r.t. for the specified time. Samples were taken periodically and injected off-line into a GC equipped with a DB-5 capillary column and an FID detector. Product yields and purities were determined by a combination of GC analysis and ^{1}H NMR spectroscopy. The products were identified by MS and by ^{1}H NMR spectroscopy.

Acknowledgment

The authors wish to thank EPSRC and Johnson-Matthey Plc. for funding this study.

References

(1) Figueras, F. *Top. Catal.* **2004**, *29*, 189.
(2) Hattori, H. *J. Jpn. Pet. Inst.* **2004**, *47*, 67.
(3) Hattori, H. *Chem. Rev.* **1995**, *95*, 537.
(4) Corma, A.; Fornes, V.; Martin-Aranda, R. M.; Garcia, H.; Primo, J. *Appl. Catal.* **1990**, *59*, 237.
(5) Barthomeuf, D.; Coudurier, G.; Vedrine, J. C. *Mater. Chem. Phys.* **1988**, *18*, 553.
(6) Martens, L. R.; Grobet, P. J.; Jacobs, P. A. *Nature (London, U.K.)* **1985**, *315*, 568.
(7) Kim, J. C.; Li, H.-X.; Chen, C.-Y.; Davis, M. E. *Microporous Mater.* **1994**, *2*, 413.
(8) Kloestra, K. R.; Van Bekkum, H. *Stud. Surf. Sci. Catal.* **1997**, *105A*, 431.
(9) Suzukamo, G.; Fukao, M.; Hibi, T.; Tanaka, K.; Chikaishi, K. In *Proceedings of the International Symposium on Acid-Base Catalysis, Sapporo, 1988*; Tanabe, K.; Hattori, H.; Yamaguchi, T., Eds.; Kodansha Ltd.: Tokyo, **1989**, 405.
(10) Corma, A.; Martin-Aranda, R. M. *Appl. Catal., A* **1993**, *105*, 271.
(11) Corma, A.; Fornés, V.; Martín-Aranda, R. M.; Rey, F. *J. Catal.* **1992**, *134*, 58.
(12) Guida, A.; Lhouty, M. H.; Tichit, D.; Figueras, F.; Geneste, P. *Appl. Catal., A* **1997**, *164*, 251.
(13) Corma, A.; Iborra, S.; Miquel, S.; Primo, J. *J. Catal.* **1998**, *173*, 315.
(14) Abrouki, Y.; Zahouily, M.; Rayadh, A.; Bahlaouan, B.; Sebti, S. *Tetrahedron Lett.* **2002**, *43*, 8951.
(15) Zahouily, M.; Bahlaouan, B.; Aadil, M.; Rayadh, A.; Sebti, S. *Org. Process Res. Dev.* **2004**, *8*, 275.
(16) Zahouily, M.; Abrouki, Y.; Bahlaouan, B.; Rayadh, A.; Sebti, S. *Catal. Commun.* **2003**, *4*, 521.
(17) Bennazha, J.; Zahouily, M.; Sebti, S.; Boukhari, A.; Holt, E. M. *Catal. Commun.* **2001**, *2*, 101.
(18) Grange, P.; Bastians, P.; Conaec, R.; Marchand, R.; Laurent, Y. *Appl. Catal., A* **1994**, *114*, L191.
(19) Climent, M. J.; Corma, A.; Fornés, V.; Frau, A.; Guil-López, R.; Iborra, S.; Primo, J. *J. Catal.* **1996**, *163*, 392.
(20) Moison, H.; Texier-Boullet, F.; Foucaud, A. *Tetrahedron* **1987**, *43*, 537.
(21) Aguilera, A.; Alcantara, A. R.; Marinas, J. M.; Sinisterra, J. V. *Can. J. Chem.* **1987**, *65*, 1165.
(22) Veldurthy, B.; Clacens, J. M.; Figueras, F. *Adv. Synth. Catal.* **2005**, *347*, 767.
(23) Choudary, B. M.; Kantam, M. L.; Kavita, B.; Reddy, C. V.; Figueras, F. *Tetrahedron* **2000**, *56*, 9357.
(24) Choudary, B. M.; Kantam, M. L.; Neeraja, V.; Rao, K. K.; Figueras, F.; Delmotte, L. *Green Chem.* **2001**, *3*, 257.
(25) Reddy, T. I.; Varma, R. S. *Tetrahedron Lett.* **1997**, *38*, 1721.
(26) Tanabe, K.; Hoelderich, W. F. *Appl. Catal., A* **1999**, *181*, 399.
(27) Jones, G. *Org. React. (N.Y.)*, Vol. 15; Cope, A. C., Ed.; Wiley: New York, **1967**.

(28) Bergman, E. D.; Ginsburg, D.; Pappo, R. *Org. React. (N.Y.)*, Vol. 10; Adams, R.; Blatt, A. H.; Boekelheide, V.; Cope, A. C.; Curtis, D. Y.; Mcgrew, F. C.; Niemann, C., Eds.; Wiley: New York, **1959**, 179.

(29) Pines, H.; Stalick, M. *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds*; Academic Press: New York, **1977**, 234.

(30) Chalais, S.; Laszlo, P.; Mathy, A. *Tetrahedron Lett.* **1985**, *26*, 4453.

(31) Choudary, B. M.; Kantam, M. L.; Reddy, C. V.; Rao, K. K.; Figueras, F. *J. Mol. Catal. A: Chem.* **1999**, *146*, 279.

(32) Gacia-Raso, A.; Garcia-Raso, J.; Campaner, B.; Mestres, R.; Sinisterra, J. V. *Synthesis* **1982**, 1037.

(33) Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, New York, **1979**, 61.

(34) Brown, M. D.; Nelson, W. J.; Turner, R. J.; Walmsley, D. G. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 337.

(35) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1993**, *115*, 2348.

(36) Climent, M. J.; Corma, A.; Iborra, S.; Velty, A. *J. Mol. Catal. A: Chem.* **2002**, *182-183*, 327.

(37) Costantino, U.; Curini, M.; Montanari, F.; Nocchetti, M.; Rosati, O. *J. Mol. Catal. A* **2003**, *195*, 245.

(38) Reddy, T. I.; Varma, R. S. *Tetrahedron Lett.* **1997**, *38*, 1721.

(39) Saito, T.; Gato, H.; Honda, K.; Fujii, T. *Tetrahedron Lett.* **1992**, *33*, 7535.

(40) Yamawaki, J.; Kawate, T.; Ando, T.; Hanafusa, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1885.

(41) Sebti, S.; Nazih, R.; Tahir, T.; Salhi, L.; Saber, A. *Appl. Catal., A* **2000**, *197*, L187.

(42) Rao, P. S.; Venkataratnan, R. V. *Tetrahedron Lett.* **1991**, *32*, 5821.

(43) Macquarrie, D. J.; Clark, J. H.; Lambert, A.; Mdoe, J. E. G.; Priest, A. *React. Funct. Polym.* **1997**, *35*, 153.

(44) Cabello, J. A.; Campelo, J. M.; Garcia, A.; Luna, D.; Marinas, J. M. *J. Org. Chem.* **1984**, *49*, 5195.