Activity of Alkaline and Alkaline-Earth Carbonates as Heterogeneous Catalysts for the Knoevenagel Condensation between Benzaldehyde and Malononitrile

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This paper reports the results obtained in the Knoevenagel condensation between benzaldehyde and malononitrile using various alkaline and alkaline-earth carbonates as catalysts. Within each carbonate series, the catalyst basicity increases with increasing ionic radius of the metal. Also, the catalytic activity increases with increase in the solid basicity.

Basic catalysts are receiving much attention lately as they facilitate a variety of organic processes that take place via carbanionic intermediates. Some are also used in fine chemistry processes. This type of solid includes oxides,[1,2] hydroxides,[3] zeolites,[4] organic resins,[5] sepiolites,[6] hydrotalcites,[7] and modified aluminium orthophosphate systems,[8] among others. Some of the primary applications of these solids are in condensations of carbonyl compounds,[9-11] as well as Knoevenagel reactions[12] and retroaldolization,[13] the latter two of which have been used to assess the basicity of the solid catalysts concerned.

Alkaline and alkaline-earth carbonates have so far scarcely been used as solid catalysts in gas phase. The low thermal stability of some precludes use at temperatures above 400 °C. However, they are useful for liquid-phase organic syntheses.[14,15] Some alkaline carbonates have been used for doping alumina[16] and metal orthophosphates.[17]

In this work we studied the catalytic activity of various carbonates in the Knoevenagel condensation between benzaldehyde and malononitrile. For this purpose, we used the following commercially available alkaline and alkaline-earth carbonates: Li_2CO_3 (Panreac ref. 141391), Na_2CO_3 (Panreac ref. 141648), K_2CO_3 (Panreac ref. 141490), Cs_2CO_3 (Aldrich ref. 20,212-6), $CaCO_3$ (Probus ref. 41710), $SrCO_3$ (Aldrich ref. 28,983-3) and $BaCO_3$ (Panreac 131181). Prior to use, all solids were activated by calcination at an increasing temperature: 200 °C, 300 °C, 400 °C and 500 °C, which were kept for 1 h each. The TGA and XRD patterns obtained after calcination showed none to decompose within the temperature range studied. Also, their S_{BET} never exceeded 2 $m^2\ g^{-1}$.

The basicity of the solids was determined by using a spectrophotometric procedure[18] involving measurement of the amount of titrant (phenol,$pK_a = 9.9$) adsorbed in monolayer form by each solid from the isotherm (25 °C) obtained on immersion of various amounts of solid in cyclohexane solutions containing a variable known amount of phenol. The amount of titrant remaining in solution (in equilibrium with the adsorbed phase) was determined at the maximum absorption wavelength for the titrant ($\lambda_{max} = 271.6$ nm). The results thus obtained were fitted to the following Langmuir equation:

$$\frac{C}{X}=\frac{1}{X_m b}+\frac{C}{X_m}$$

in order to calculate X_m from the slope of a C/X *vs* plot (C is the concentration of titrant in equilibrium with the adsorbed phase, X; b is the Langmuir constant, which represents the strength of the substrate-active site interaction; and X_m is the amount of titrant adsorbed in monolayer form). The substrate-active site adsorption stoichiometry for moderately basic solids in dilute titrant solutions can be assumed to be 1:1. Under these conditions, the amount of titrant in the adsorbed monolayer will be a measure of the surface basicity of the solid.[18]

Table 1 gives the basicity values obtained for the carbonates studied. As can be seen, the solid basicity increased with the ionic radius of the metal for both alkaline and alkaline-earth carbonates.

All reactions were carried out in a flask that was fitted with a reflux condenser. The flask was immersed in a thermostated bath containing polyethylene glycol 400 and the reaction mixture was stirred magnetically. In the flask was placed an equimolar mixture (15.88 mmol) of previously distilled benzaldehyde (Merck ref. 801756) and malononitrile (Aldrich ref. M140-7), plus 24 ml of 1,4-dioxane (Merck 3115) as solvent. When the mixture reached a temperature of 90 °C, an amount of 0.546 g of the carbonate concerned was added (t = 0). Samples of the reaction mixture were then withdrawn periodically for gas chromatographic analysis using an SPB-5 60 m × 0.25 mm ID phenylsilicone capillary column and raising the temperature from 150 to 280 °C at 15 °C min^{-1}. Quantitative determinations were based on calculated response factors for binary and ternary mixtures of the reaction ingredients. The identity of each reaction product was confirmed by ^{1}H-NMR and MS. The reaction always yielded benzylidenemalononitrile selectively (no Michael addition byproduct was detected). On completion of the reaction, highly pure benzylidenemalononitrile could be isolated simply by evaporating the solvent.

The reaction involved is as follows:

$$C_6H_5\text{-COH} + CH_2\text{-(CN)}_2 \rightarrow C_6H_5\text{-CH=C-(CN)}_2 + H_2O$$

No hydroxilated intermediate was detected.

Figure 1 shows the variation of conversion as a function of the reaction time for the carbonates studied. The results for $CaCO_3$ and $SrCO_3$ (X_T < 2%, t = 120 min) have been omitted. The best results were provided by K_2CO_3 and Cs_2CO_3; the slightly falling portion in the curves was the result of retrocondensation at high yields, which reflected in a small increase in the amount of benzaldehyde present in the reaction medium.

Corma *et al.*[19] studied in depth the condensation of various carbonyl compounds (cyclohexanone, benzophenone, *p*-aminoacetophenone) and substances including active methylene units of the type X-CH_2-Y (X,Y = CN, COOEt) over sepiolites, zeolites and hydrotalcites. They carried out a kinetic study of the process and found the reaction rate to conform to Langmuir kinetics, *i.e.* the reaction rate to depend on the nature of the carbonyl and methylene-containing compound. The slow

Table 1. Relationship between the solid catalytic activity (r_a) and basicity. All solids were calcined at 773 K

Catalyst	Basic Sites/ 10^{-7} mol g^{-1}	r_a/ 10^{-2} mol s^{-1} g^{-1}
Li_2CO_3	2	0.18
Na_2CO_3	2	2.97
K_2CO_3	11	29.14
Cs_2CO_3	20	52.14
$CaCO_3$	1	-
$SrCO_3$	1	-
$BaCO_3$	8	1.83

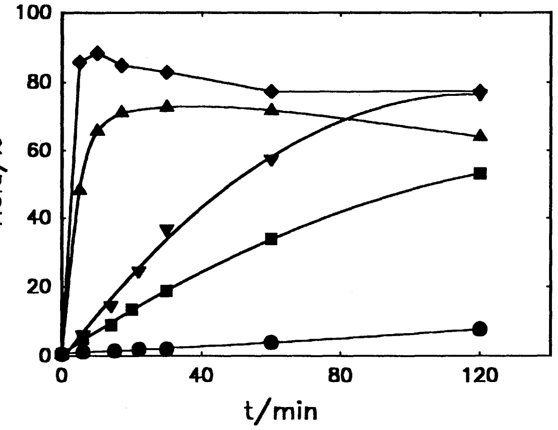

Figure 1. Variation of the reaction yield (% mol) as a function of time in the condensation between benzaldehyde and malononitrile, catalysed by Li_2CO_3 (●), $BaCO_3$ (■), Na_2CO_3 (▼), K_2CO_3 (▲) and Cs_2CO_3 (◆).

step of the process is the attack of the X-CH$^-$-Y anion, formed by the uptake of a proton at a basic site of the catalyst, on the carbonyl compound. Our kinetic tests were consistent with these findings of Corma *et al.*.[19] For a given carbonyl compound, the reaction rate depends on the amount of X-CH$^-$-Y..cat. present, which in turn must be related to the number of basic sites of the solid. Sinisterra *et al.*[9] obtained chalcone by condensation between benzalacetophenone and diethyl malonate on $Ba(OH)_2$ doped with a metal halide; they found the amount of Michael addition product obtained to be proportional to the basic strength of the solid.

Even though clear-cut quantitative relations are not always obtained, there are reported examples of other condensations on basic solids.[20] Also, the process is known to be catalysed by bases in a homogenous phase.

Our results also appear to be consistent with the assumption that the process is catalysed via the basic sites of the solid.

Table 1 gives the initial reaction rate values obtained from the slope of the curves in Fig. 1. As can be seen, there was good correlation between the reaction rate and the basicity of each solid for both the alkaline and the alkaline-earth carbonates. Because the pK_a for malononitrile is 11.0, converting this compound to its carbanion requires the presence of strong basic sites in the catalyst. The carbonates of metals of a large ionic radius must possess basic sites of a greater strength than those of smaller radii. This was indeed the case for the alkaline and alkaline-earth carbonates within each series. However, after the carbanion is produced, no Michael addition takes place —not even if excess malononitrile is used.

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