

Solid Base-catalysed Rearrangement of Methacrylonitrile to Crotononitrile

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MgO and CaO catalysts have shown high activity for the formation of crotononitrile (*cis/trans* = 6/4) in the rearrangement of methacrylonitrile.

Recently, we reported that magnesium oxide, activated by metal ions, catalysed the vapour-phase condensation of methanol with saturated ketones, esters, or nitriles to form the corresponding α,β -unsaturated compounds.¹⁻⁵ For example, methacrylonitrile can be synthesized selectively (>95%) with methanol and propionitrile over the Mn^{II} ion-containing magnesium oxide catalyst. Interestingly, trace amounts of *cis*- and *trans*-crotononitriles which are the structural isomers of methacrylonitrile were found in the products. Mechanistically, the above-mentioned reaction is similar to aldol type condensation, the C-C bond formation generally taking place at the α -position to form the iso-compound, so that the formation of crotononitrile is unusual.⁶ From separate experiments, we found that the rearrangement of methacrylonitrile to crotononitrile readily occurred catalytically over solid base metal oxides, and we now report our results.

This rearrangement was demonstrated with various metal oxide catalysts having basic or acidic properties. Unless noted otherwise, the catalysts used were commercially available materials. Catalytic activity was determined using a pulse reactor connected directly to a gas chromatograph (PEG 1000, 2 m, 70 °C). The catalysts (50 mg) were treated at 600 °C for 2 h under a He gas stream prior to reaction and then the reactant (pulse size 1 μ l) was introduced into the reactor at the desired temperature. Products were identified by g.c.-m.s. and ¹H n.m.r. spectroscopy.

Table 1 summarizes the selectivity of the rearrangement of methacrylonitrile to crotononitrile. No reaction occurred in the absence of catalyst under the reaction conditions shown in Table 1. Among the catalysts tested, CaO, MgO, and La₂O₃, which are commonly known as strong solid bases, were found

Table 1. Rearrangement of methacrylonitrile to crotononitrile over various metal oxide catalysts.^a

Run number	Catalyst	Conversion ^b (%)	Selectivity (%) ^b	
			<i>cis</i>	<i>trans</i>
1	CaO	7.7	59.4	40.6
2	CaO ^c	21.5	40.5	30.6
3	MgO	5.5	57.4	42.6
4	MgO ^c	16.0	58.2	41.8
5	La ₂ O ₃	0.5	66.9	33.1
6	SrO	0	—	—
7	ZnO	0	—	—
8	SnO ₂	0	—	—
9	Al ₂ O ₃	5.7	0	0
10	SiO ₂ -Al ₂ O ₃	2.8	0	0

^a Reaction temperature, 320 °C; catalyst weight, 50 mg; pulse size, 1 μ l; carrier gas (He), 50 ml min⁻¹. ^b The values were calculated for the reaction of the fifth pulse. ^c Prepared from CaCO₃ and Mg(OH)₂.

to be particularly active for methacrylonitrile rearrangement (Runs 1, 3, 5). The crotononitrile was a mixture of *cis*- and *trans*-isomers with a *cis/trans* ratio of 6/4, which is the thermodynamic equilibrium composition at the reaction temperature. Trace amounts of allyl cyanide were also formed. Total carbon balance was close to 100% in each pulse with the exception of the initial one. With weak basic oxide catalysts such as ZnO (Run 7) and SnO₂ (Run 8), no reaction occurred at all. On the other hand, with the acidic catalysts, Al₂O₃ (Run 9) and/or Al₂O₃-SiO₂ (Run 10), methacrylonitrile was converted slightly but crotononitrile was not formed. No products were found in the outlet of the reactor; therefore the reacted methacrylonitrile seems to be retained on the surface of the catalyst in a polymeric state. It is, therefore, concluded that the rearrangement of methacrylonitrile is promoted in the presence of metal oxide catalysts which are strong bases.

In order to confirm the catalytic performance of the basic metal oxide further, we prepared CaO (Run 2) and MgO (Run 4) by the calcination of CaCO₃ and Mg(OH)₂ respectively at 600 °C. Both catalysts have larger surface areas and showed higher activities than the commercially available oxides (Table 1). Marked deactivations were observed for both catalysts. This may be due to the poisoning of the strong surface base site by the deposition of carbonaceous species because small amounts of acetonitrile and propionitrile were detected during elution.

The rearrangements of isobutyronitrile and pent-3-enenitrile were carried out using the MgO catalyst under the same conditions used for the methacrylonitrile conversion, in order to inspect the reaction pathway. *n*-Butyronitrile was not produced during the reaction of isobutyronitrile. In the case of the pent-3-enenitrile rearrangement, 2- and 3-methylbutene-2-nitrile which form only *via* alkyl migration were not detected at all in the products. These results suggest the possibility that

the reaction path involves a π -allyl intermediate formed by methyl hydrogen abstraction by the surface base site and a CN-migration. Furthermore, this type of rearrangement seems to be specific for unsaturated nitriles, since the rearrangement of 2-phenylpropene did not occur. However, further examination is required before the reaction path can be fully understood.

Finally, catalyst screening was performed using various magnesium compounds as catalysts in order to discover a more effective catalyst for the title reaction. As a result, basic magnesium carbonate was found to be an effective and promising catalyst. The conversion and selectivity data obtained with a fixed bed flow-reactor were as follows; the selectivity to crotononitrile was 90% (*trans*-form 35%, *cis*-form 55%) at 20% conversion of methacrylonitrile (reaction temperature, 320 °C; catalyst weight, 1 g; space velocity, 43 ml min⁻¹ g-catalyst⁻¹; feed composition, He:methacrylonitrile = 12:1).

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