

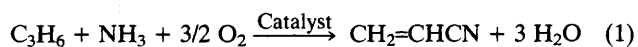
Selective Formation of Acrylonitrile *via* Oxidative Methylation of Acetonitrile with Methane over Superbasic Catalysts

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Promotion of CaO or MgO with various binary alkali metal compounds such as NaA + CsA, KA + CsA, LiA + CsA or LiA + NaA, where A = SO₄²⁻, OH⁻, Cl⁻, AcO⁻, CO₃²⁻ or NO₃⁻, leads to highly basic (superbasic) catalysts, which exhibit a noticeable synergistic effect compared with the effect produced by any monoalkali promoted system in the selective formation of acrylonitrile *via* oxidative methylation of acetonitrile with methane.

Acrylonitrile is widely used as a monomer, and is produced commercially by the vapour-phase catalytic propylene ammoxidation process developed by Sohio¹ [eqn. (1)].



Because of the large price difference between propylene and methane and the dependence of the former on crude oil fractions, a methane-based process seems to be attractive. A process for the production of acrylonitrile *via* catalytic oxidative methylation of acetonitrile with methane was suggested more than twenty years ago.^{2,3} Silica supported metal halides of Groups 1 and 2, antimony oxide and molybdenum oxide were employed as catalysts, but the details regarding the catalysts have not been disclosed.

We recently reported⁴⁻⁶ that a substantial synergistic effect is obtained in the oxidative methylation of toluene with methane to styrene and ethylbenzene and also in the oxidative coupling of methane to ethylene and ethane over bialkali-promoted MgO or CaO compared with the effects produced by the monoalkali-promoted substrates. This was attributed to the synergistic increase in the surface basicity (superbasicity) caused by the high enrichment of the surface layer with the bialkali ions. In this communication, we demonstrate that acrylonitrile is formed with higher selectivity and yield *via* oxidative methylation of acetonitrile with methane if the reaction is carried out over bialkali-promoted CaO or MgO, instead of the monoalkali-promoted substrates.

The catalysts have been prepared as follows: CaO or MgO powder, either prepared by the sol-gel method or obtained

commercially (Aldrich), was impregnated with an aqueous solution of mono (LiA, NaA, KA, RbA or CsA, where A = SO₄²⁻, OH⁻, Cl⁻, AcO⁻, CO₃²⁻ or NO₃⁻) or bialkali (LiA + NaA, LiA + CsA, NaA + CsA, KA + CsA *etc.*) metal compounds, keeping the total alkali metal content 10 mol% (equimolar amount for the bialkali). This was followed by evaporation to dryness, drying overnight at 120 °C, calcination in air at 750 °C for 15 h, powdering, pressing, crushing and sieving to 80 mesh particle sizes. No significant differences in the catalytic performance were observed between the catalysts prepared by the sol-gel method and those obtained commercially. The catalytic runs were carried out under atmospheric pressure and at 750 °C in a fixed bed horizontal-flow reactor constructed from a high purity alumina tube (i.d. 6 mm) packed with 200 mg of catalyst and mounted inside a small programmable tube furnace. The reactant gas mixture of methane, oxygen and helium (diluent) at a total flow rate of 50 ml min⁻¹ (NTP) was passed through an acetonitrile vapour saturator maintained at 25 °C just before the inlet of the reactor, giving partial pressure ratios, $P(\text{CH}_4):P(\text{O}_2):P(\text{MeCN}):P(\text{He})$ of 5.0:1.0:1.5:6.5 and a space velocity of 15 000 cm³ g⁻¹ h⁻¹ (NTP). The products were analysed on-line by a GC (PE Sigma 2000) fitted with flame-ionization and thermal-conductivity detectors and a 10-port sampling valve connected to Chromosorb 102 (3.20 mm × 3.64 m) and Porapak Q columns (3.20 mm × 1.82 m). Some selected runs were analysed by a GC-MS (HP5890) fitted with a mass-selective detector (5971A). The catalysts were characterized by surface area determination, basicity and base strength measurements, and X-ray photoelectron spectroscopy (XPS).

Table 1 Catalytic performance for oxidative methylation of acetonitrile with methane in the empty reactor and over unpromoted and mono- or bi-alkali-promoted CaO^a

Catalyst ^b (alkali loading in mol%)	Conversion (mol%)			Selectivity ^c (mol%)			Yield (%)		
	CH ₄	O ₂	MeCN	EtCN	CH ₂ =CHCN	HCN	CO _x x = 1,2	CH ₂ =CHCN	EtCN
None	<1.0	32.0	8.5	2.0	7.0	31.0	57.0	0.6	0.2
Quartz wool	1.4	35.0	9.0	3.0	9.0	30.0	54.0	0.8	0.3
CaO	2.8	69.0	16.0	5.0	16.0	24.0	48.0	2.6	0.8
10% Li ⁺ /CaO	4.2	75.0	20.0	6.0	33.0	18.0	39.0	6.6	1.2
10% Na ⁺ /CaO	5.8	88.0	22.0	7.0	39.0	16.0	34.0	8.6	1.5
10% K ⁺ /CaO	3.7	78.0	19.0	5.0	29.0	20.0	40.0	5.5	1.0
10% Rb ⁺ /CaO	3.5	80.0	18.0	4.0	27.0	22.0	41.0	4.9	0.7
10% Cs ⁺ /CaO	5.0	85.0	21.0	6.0	37.0	17.0	35.0	7.8	1.3
(5% Li ⁺ + 5% Na ⁺)/CaO	9.4	90.0	32.0	8.0	60.0	10.0	20.0	19.2	2.6
(5% Li ⁺ + 5% K ⁺)/CaO	8.7	92.0	28.0	6.0	55.0	12.0	24.0	15.4	1.7
(5% Li ⁺ + 5% Rb ⁺)/CaO	8.0	90.0	29.0	6.0	51.0	13.0	25.0	14.8	1.7
(5% Li ⁺ + 5% Cs ⁺)/CaO	10.0	93.0	33.0	7.0	61.0	11.0	19.0	20.1	2.3
(5% Na ⁺ + 5% K ⁺)/CaO	8.2	89.0	30.0	7.0	56.0	12.0	21.0	16.8	2.1
(5% Na ⁺ + 5% Rb ⁺)/CaO	7.8	90.0	28.0	6.0	53.0	14.0	23.0	14.8	1.7
(5% Na ⁺ + 5% Cs ⁺)/CaO	12.0	94.0	36.0	9.0	70.0	5.0	14.0	25.2	3.2
(5% K ⁺ + 5% Rb ⁺)/CaO	8.0	96.0	27.0	7.0	54.0	13.0	21.0	14.6	1.9
(5% K ⁺ + 5% Cs ⁺)/CaO	11.0	92.0	31.0	8.0	69.0	6.0	15.0	21.4	2.5
(5% Rb ⁺ + 5% Cs ⁺)/CaO	8.3	95.0	28.0	5.0	51.0	15.0	22.0	14.3	1.4

^a Reaction conditions: $T = 750\text{ }^{\circ}\text{C}$, $P = 1\text{ atm}$, total flow = 50 ml min^{-1} (NPT), $P(\text{CH}_4) : P(\text{O}_2) : P(\text{C}_7\text{H}_8) : P(\text{He}) = 5.0 : 1.0 : 1.5 : 6.5$ and space velocity = $1.5 \times 10^4\text{ cm}^3\text{ g}^{-1}\text{ h}^{-1}$. Results are after 2 h of reaction. ^b The catalysts were prepared from M_2SO_4 precursors ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$ or Cs); the surface areas of the samples were less than $10\text{ m}^2\text{ g}^{-1}$. ^c The yield is calculated on the basis of the moles of acetonitrile converted.

The major products of the oxidative methylation of acetonitrile are acrylonitrile, propionitrile, hydrogen cyanide, carbon dioxide and carbon monoxide with small amounts of ethylene, ethane and water and trace amounts of unidentified compounds. The results obtained in the absence and the presence of unpromoted and mono- or bi-alkali promoted CaO (prepared from the alkali sulfate precursors) at $750\text{ }^{\circ}\text{C}$ are presented in Table 1. In the blank reactor (without or with quartz wool) some reaction took place, carbon oxides and hydrogen cyanide being, however, the dominant products. A small yield 0.6–0.8% of acrylonitrile was obtained, indicating that some methylation and, possibly, disproportionation of acetonitrile occurred homogeneously. The latter reaction (disproportionation) was confirmed by carrying out the reaction in the absence of methane, which resulted in a much smaller yield of acrylonitrile. Unpromoted CaO (calcined, $900\text{ }^{\circ}\text{C}$, 15 h, surface area $9\text{ m}^2\text{ g}^{-1}$) showed somewhat better performances than those obtained in the blank runs. The acetonitrile conversion increased and the selectivities to acrylonitrile and propionitrile also increased whereas those to carbon oxides and hydrogen cyanide decreased to some extent. This indicates that a substrate with basic properties is useful for the process. This was confirmed by replacing CaO with SiO_2 (Aldrich, $600\text{ m}^2\text{ g}^{-1}$), which shows a negligible conversion and acrylonitrile selectivity.

Upon promoting CaO with any of the monoalkali compounds (the surface area of the resulting materials decreased to $5\text{--}6\text{ m}^2\text{ g}^{-1}$), the conversions of all three reactants and the selectivities to acrylonitrile and propionitrile increased compared with the results obtained over unpromoted CaO. The selectivities to carbon oxides and hydrogen cyanide decreased further. Among the five mono-alkali-promoted systems, the highest acrylonitrile yield (8.6%) was obtained over 10 mol% Na^+ /CaO and the lowest (4.9%) over 10 mol% Rb^+ /CaO. We suggest that this enhancement of the catalytic performances is due to an increase in the basicity caused by the promotion of CaO with the monoalkali compound.

Significant increases in the conversions of acetonitrile and, particularly, in the selectivities to acrylonitrile were observed over all bi-alkali metal compound (equimolar quantities) promoted CaO, although the surface area of the resulting

catalysts was the lowest ($3\text{--}4\text{ m}^2\text{ g}^{-1}$). The methane and oxygen conversions and the selectivities to propionitrile also showed some increase, while the selectivities to carbon oxides and hydrogen cyanide drastically decreased. An acrylonitrile yield as high as 25.2% was obtained over (5 mol% Na^+ + 5 mol% Cs^+)/CaO at $750\text{ }^{\circ}\text{C}$. Other bi-alkali-promoted systems also showed noticeable increases in the acetonitrile conversion and in the acrylonitrile selectivity. The least effective among these systems, however, was (5 mol% Rb^+ + 5 mol% Cs^+)/CaO with an acrylonitrile yield of 14.3% (which is still much higher than those over any monoalkali promoted CaO). During the catalytic reaction a substantial coke formation was observed on all the catalysts, particularly on the bi-alkali-promoted CaO. The overall carbon mass balance for 60 h was about 85%. In spite of the coke formation, the selectivity to acrylonitrile, after an initial increase for 2 h, remained unchanged with time-on-stream (for 60 h). This seems to suggest that the coke deposition on the catalyst plays a role in the formation of acrylonitrile via oxidative methylation of acetonitrile.

The bi-alkali-promoted CaO catalysts prepared from other than the SO_4^{2-} precursors, namely OH^- , Cl^- , AcO^- , CO_3^{2-} or NO_3^- , also showed much higher performances than those obtained over the respective mono-alkali-promoted systems. However, the best results have been obtained over the catalysts prepared from the SO_4^{2-} precursors (Table 1). The differences among the bi-alkali catalysts from different anions are small but not negligible. While the nature of the anion exerts some influence on the catalytic performance, the major role is played by the nature of the bi-alkali cations. By replacing CaO with MgO, similar enhanced performances were observed over the bi-alkali-promoted systems but to a somewhat smaller extent.

The synergistic catalytic effect of the bi-alkali-promoted CaO systems in the oxidative methylation of acetonitrile compared with the respective monoalkali-promoted systems is reflected in the synergistic increase of the basicity and base strength distribution of the catalysts as measured by the gaseous CO_2 adsorption followed by its stepwise thermal desorption (STD) and by the benzoic acid titration methods. The STD method revealed that the largest amount of CO_2

(2400–3000 $\mu\text{mol g}^{-1}$) is also desorbed from the bialkali-promoted CaO systems, indicating that these systems possess the highest basicity. More importantly, the basicity is the highest in the range of 700–850 °C, which is close to the reaction temperature. The benzoic acid titration method showed that most of the bialkali-promoted systems have a noticeable base strength in the range of $26 \leq H_- \leq 35$ (H_- is the base strength = $\text{p}K_a$ of the indicator), unlike the monoalkali-promoted systems which do not show any basicity in this range. This indicates that the bialkali-promoted systems are superbases, according to the classification of Tanabe *et al.*⁷

The high basicity of the bialkali-promoted CaO is, presumably, due to the high enrichment of the surface with the alkali ions, unlike the monoalkali-promoted systems, as evidenced by XPS studies. For the ($\text{Na}^+ + \text{Cs}^+$)/CaO systems, the surface concentration of Na and Cs increased 7- and 3-fold, respectively, after the catalytic reaction. Apparently, the high catalytic performance of the bialkali-promoted CaO

systems is related to their high basicity (superbasicity) caused by the high surface enrichment with the alkali ions.

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