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Synergistic Effects of Superbasic Catalysts on the Selective Formation of Acrylonitrile via Oxidative Methylation of Acetonitrile with Methane

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The oxidative methylation of acetonitrile with methane to acrylonitrile occurs more actively and selectively over bialkali promoted CaO catalysts than over any monoalkali promoted system. The most effective catalytic systems are obtained with Li*A* + Cs*A*, Na*A* + Cs*A*, or K*A* + Cs*A* (*A* = SO_4^{2-}, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-) supported on CaO, containing total alkali loadings of 10 mol% with equal molar amounts of both alkalis. At 750°C, under atmospheric pressure, at $CH_4:O_2:CH_3CN:He$ partial pressure ratios of 5.0 : 1.0 : 1.5 : 6.5, and at a space velocity of 15,000 $cm^3\ g^{-1}\ h^{-1}$, the highest selectivity to acrylonitrile (70.0 mol%) and yield (25%) are obtained over (5 mol% Na^+ + 5 mol% Cs^+)/CaO (prepared from the sulfate precursors). Any bialkali-promoted system containing Rb was less effective, whereas the Li-containing systems, though active initially, gradually lost the activity due to its volatility. The performances of the effective bialkali systems, after an initial increase, remained almost unchanged for a period of 60 h. In contrast, the stability of any monoalkali promoted system with time-on-stream was very low and the maximum initial yield of acrylonitrile was only 11.5% under the aforementioned conditions. The synergistic increase in the catalytic performance of the bialkali promoted CaO is reflected in the synergistic increase of the surface basicity (leading to superbasicity) caused by the high enrichment of the surface layer with the alkali ions. The relationship between the catalytic performances and the physicochemical characteristics of the catalysts revealed by XPS, AAS, and basicity measurements is explored. © 1994 Academic Press, Inc.

INTRODUCTION

Due to an inevitable depletion of crude oil, many groups are conducting extensive research to replace crude-oil-based chemicals with abundant natural gas and coal-based chemicals. The direct partial oxidation of methane to higher hydrocarbons or oxygen-containing chemicals is an attractive route for utilizing natural gas. In recent years the oxidative coupling of methane to C_2 hydrocarbons has received a great deal of attention, and a wide range of metal-oxide-based catalysts have been reported to exhibit good performances (1–5). However, this direct process has yet to acquire practical importance in view of a number of obstacles, such as a lack of highly effective catalysts, the requirement of high reaction temperatures, etc., still prevailing. An alternative approach would be the utilization of methane with other chemicals, such as toluene, acetonitrile, or isobutene, to produce important monomers like styrene, acrylonitrile, or isoprene, respectively, in the presence of oxygen and catalysts (6).

In view of the tremendous growth in its use as a starting material for a wide range of products, acrylonitrile has become one of the 50 most important chemicals. It is produced commercially by the vapor-phase catalytic propylene ammoxidation process developed by Sohio (7), according to the reaction

$$C_3H_6 + NH_3 + 3/2\,O_2 \xrightarrow{\text{catalyst}} CH_2 = CHCN + 3H_2O.$$

However, because of the large price difference between propylene and methane and the dependence of the former on petroleum, a methane-based process may eventually be of interest. Such a process for the production of acrylonitrile via catalytic oxidative methylation of acetonitrile with methane was suggested a few years ago (8, 9). The reaction involves the high temperature (700–800°C) interaction of methane with compounds containing a methyl group at an α-position on an electron-withdrawing functional group, such as acetonitrile. The latter compound could be obtained from coal- and natural-gas-derived products, such as carbon monoxide, hydrogen, and ammonia as patented by Monsanto (10), or by the ammonolysis of acetic acid produced by methanol carbonylation over a rhodium-based catalyst (6). Consequently, a two-stage technology to manufacture acrylonitrile directly from natural gas and ammonia was proposed. The oxidative methylation of acetonitrile with methane was found to occur over a variety of catalysts such as silica supported

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halides of alkali or alkaline-earth metals, the oxides of bismuth, antimony, molybdenum or zinc, etc. (6). The best activity was exhibited by KBr/SiO_2 or $ZnNO_3/SiO_2$, but the details regarding the catalysts have not been disclosed. It is not clear whether replacing silica with some other support would give similar results.

Recently, on the basis of catalysts used for the oxidative coupling of methane to C_2 hydrocarbons, several groups have employed some methane coupling catalysts for the oxidative methylation of toluene with methane to styrene (11–15). Such studies have revealed that this reaction is catalyzed by basic oxides, such as alkaline earth metal oxides, transition metal oxides, rare earth metal oxides promoted with alkali. Particularly effective catalysts have been bialkali promoted CaO or MgO, which are superbasic (15).

The term "superbase" is used to denote a base strong enough to detach a proton from hydrocarbon molecules, such as triphenylmethane (pK_a of acid indicator = 33) or methane (pK_a = 40) (16). The base strength (denoted $H_- = pK_a$) of a superbase should therefore lie in the range $40 \geq H_- \geq 33$. More recently, Tanabe *et al.* (17) suggested that materials which possess basic sites for which $H_- \geq 26.0$ could be termed superbases. The latter definition is in conformity with that of solid superacids. A superbase can be obtained by promoting an oxide, such as MgO or Al_2O_3, with bialkali metals (16). We observed (15, 18–21) that upon promoting MgO or CaO with various bialkali metal compounds, instead of monoalkali compounds, a substantial synergistic effect is obtained in the oxidative coupling of methane to C_2 hydrocarbons and also in the oxidative methylation of toluene to styrene. This synergistic effect was attributed to the superbasicity of the catalysts caused by the enrichment of the surface layer with the alkali ions, enrichment which is very high for the bialkali promoted systems compared to the monoalkali promoted ones. The superbasic catalysts prepared via promoting MgO or CaO with various bialkali compounds such as $NaA + CsA$, $LiA + CsA$, or $KA + CsA$ ($A = SO_4^{2-}$, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-) were found to be effective in both the reactions.

Since acetonitrile contains, as toluene, a strong electron-withdrawing functional group, it is likely that similar catalysts with superbasic properties could be beneficial for the oxidative methylation of acetonitrile to acrylonitrile as well. In the present paper we show that such superbasic catalysts are indeed effective in the oxidative methylation of acetonitrile to acrylonitrile. We report on a substantial synergistic effect in the activity, selectivity and stability with time-on-stream when CaO is promoted with binary mixtures of alkali compounds, instead of the monoalkali compounds. Some preliminary results have been reported in a short communication (22).

EXPERIMENTAL

Catalyst Preparation

The details regarding the catalyst preparation have been reported previously (19, 20). Briefly, CaO obtained commercially (Aldrich), was calcined at 900°C for 15 h followed by its cooling to room temperature, pressing, crushing and sieving to 80–100 mesh particle sizes. Onto this calcined CaO powder, mono- or bialkali metal compounds were deposited by the conventional impregnation method, using one or two of six different alkali precursors obtained from Aldrich (M_2SO_4, MOH, MCl, M_2CO_3, MNO_3, or CH_3COOM, where M = Li, Na, K, Rb, or Cs). The initial alkali metal loading for the mono- or bialkali metal compounds deposition was in most cases 10 mol% with an equal molar amount of both the compounds for the latter. During calcination most of the alkali sulfate, chloride, nitrate, and acetate decomposed and the respective gases evolved out. Some lithium and rubidium were also lost from the samples as evidenced by AAS and XPS results.

Reactor Setup/Catalyst Screening

The catalytic runs were carried out in the temperature range of 650–850°C, under atmospheric pressure, in a fixed bed horizontal-flow reactor constructed of a high purity alumina tube (6 mm i.d., 30 cm long) and heated by a programmable single-zone electric furnace (Lindberg 545-142) with a built-in thermocouple. The sketch of the reactor setup is presented in Fig. 1. Usually 200 mg of calcined catalyst sandwiched between quartz wool plugs was placed in the center of the reactor tube, the hot zone being 8 cm long. The reactor tube was connected to the gas inlet and outlet systems through Cajon fittings containing O-ring seals. The reactant gas mixture of high purity methane, oxygen and helium (all 99.9% purity; Cryogenic Supply) was passed through an acetonitrile (99.5%: Aldrich) vapor saturator made of galvanized metal and maintained usually at 25°C just before the inlet of the reactor. The flow of each gas was controlled by a variable constant differential flow controller (Porter VCD1000) connected to a filter (Nupro, 7 μm) and a check valve. In most of the cases, the total flow rate of the gas mixture, measured at the outlet of the reactor, was 50 ml/min (NTP), the partial pressure ratios were $P(CH_4):P(O_2):P(CH_3CN):P(He) = 5.0:1.0:1.5:6.5$ and the space velocity was 15,000 $cm^3\ g^{-1}\ h^{-1}$ (NTP). The reactor tube was periodically cleaned with nitric acid and Erado-sol (Cambridge Chem. Prod.) to eliminate the carbonaceous and alkali materials deposited on the inside wall.

Product Analysis

The gaseous products were sampled on-line using an automatic 10-port sampling valve (Valco) and analyzed

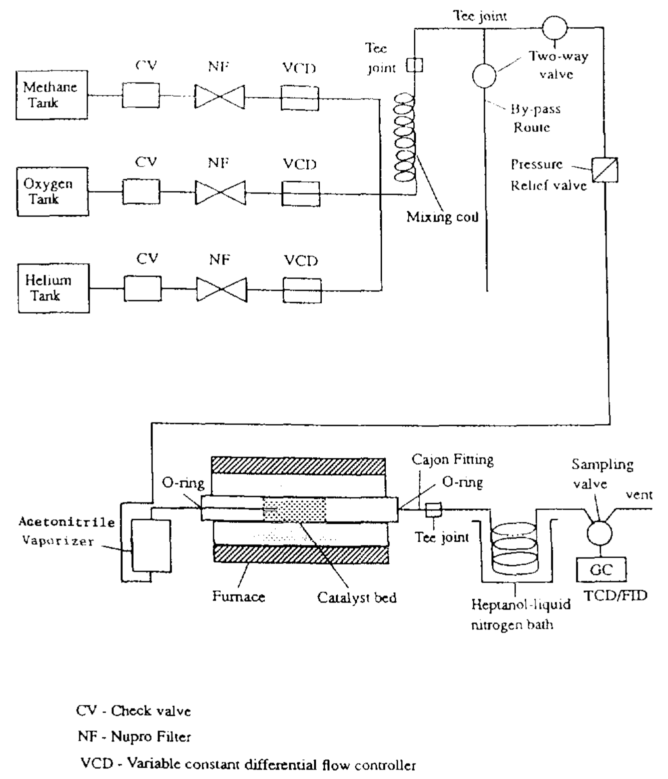


FIG. 1. Schematic diagram of the reactor setup used in the oxidative methylation of acetonitrile.

by gas chromatography (Perkin-Elmer Sigma 2000) fitted with thermal conductivity and flame ionization detectors and attached to a PE 3600 data station. The Packed columns used to separate the products were Chromosorb 102 (3.20 mm × 3.64 m) and Porapak Q (3.20 mm × 1.82 m). Some selected runs were analyzed off-line with a GC-MS (Hewlett–Packard 5890A) fitted with a mass-selective detector (5971A) and three columns: a molecular sieve 5A (3.20 mm × 1.82 m), a poraplot wide-bore capillary (0.53 mm × 27.5 m) and a cross-linked methyl silicone capillary (0.20 mm × 12.5 m). Nitrogen or argon was used as an internal standard. The conversion of acetonitrile is expressed as the fraction of moles of acetonitrile reacted and calculated from the GC areas suitably calibrated and the response factor of acetonitrile. The selectivity is defined as the ratio of the number of moles of a particular product to the total number of moles of all the products (without water). The % yield of acrylonitrile is the product of the % conversion of acetonitrile and the selectivity.

Catalyst Characterization

The catalysts were characterized by surface area measurements (BET method), X-ray diffraction (XRD) analysis, atomic absorption spectrophotometry (ASS), X-ray photoelectron spectroscopy (XPS), and basicity/base strength distribution measurements. The details of the methods have been reported previously (*19, 23*). Briefly, the surface areas of the calcined and post-catalysis samples were determined by the BET method using the adsorption of nitrogen gas at the liquid nitrogen temperature (Micromeritics 2100D). The XRD patterns of the catalytic materials were obtained with a Siemens Analytical X-ray Instrument equipped with a curved, position-sensitive detector and a CuK_α source of radiation. The JCPDS files were used to identify the phases (*24*). The alkali metal ion loadings (as oxides) on the supports were determined by the AAS flame method (Perkin-Elmer 3030). The surface compositions and the valence states of the elements present in the samples were studied by XPS using a PHI 500 spectrophotometer (*25*). The basicity and the base strength distribution of the solid catalysts were determined by two methods: benzoic acid titration in the presence of indicators (*17, 26*) and gaseous acid (CO_2) adsorption followed by its stepwise thermal desorption (STD), according to Refs. (*27, 28*). Some physicochemical properties of the samples are listed in Table 1.

TABLE 1

Physicochemical Characteristics of Mono- and Bialkali-promoted CaO[a]

No.	Sample[b]	Surface area (m^2/g)	Alkali metal loading[c] (mol%) Before calcination	After calcination
1.	CaO	9.0	—	—
2.	Li^+/CaO	5.0	10.0	1.6
3.	Na^+/CaO	5.2	10.0	9.0
4.	K^+/CaO	5.5	10.0	7.0
5.	Rb^+/CaO	5.5	10.0	2.0
6.	Cs^+/CaO	5.8	10.0	8.4
7.	$(Li^+ + Na^+)/CaO$	4.0	5.0 + 5.0	0.6 + 4.0
8.	$(Li^+ + K^+)/CaO$	4.0	5.0 + 5.0	0.5 + 3.6
9.	$(Li^+ + Rb^+)/CaO$	4.2	5.0 + 5.0	0.4 + 1.0
10.	$(Li^+ + Cs^+)/CaO$	3.0	5.0 + 5.0	0.6 + 3.8
11.	$(Na^+ + K^+)/CaO$	3.0	5.0 + 5.0	3.7 + 3.5
12.	$(Na^+ + Rb^+)/CaO$	3.2	5.0 + 5.0	4.0 + 1.2
13.	$(Na^+ + Cs^+)/CaO$	3.2	5.0 + 5.0	4.0 + 4.0
14.	$(K^+ + Rb^+)/CaO$	4.0	5.0 + 5.0	3.7 + 1.0
15.	$(K^+ + Cs^+)/CaO$	4.0	5.0 + 5.0	3.5 + 4.0
16.	$(Rb^+ + Cs^+)/CaO$	3.8	5.0 + 5.0	0.8 + 4.0

[a] The alkali metal compounds are from sulfate precursors.

[b] Crystalline phases identified by XRD are CaO only, except for sample no. 3, which showed an additional phase of Na_2SO_4.

[c] Determined by AAS.

TABLE 2

Catalytic Performance for Oxidative Methylation of Acetonitrile with Methane at 750°C over Mono- or Bialkali Metal Sulfate Promoted CaO[a]

Catalyst (alkali loading in mol%)	Conversion (mol%)			Selectivity (mol%)				Yield (%)	
	CH_4	O_2	CH_3CN	CH_3CH_2CN propionitrile	$CH_2{=}CHCN$ acrylonitrile	HCN	CO_x (x = 1, 2)	$CH_2{=}CHCN$	CH_3CH_2CN
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	2.9
(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: temperature 750°C, pressure 1 atm, $P(CH_4):P(O_2):P(CH_3CN):P(He)$ = 5.0:1.0:1.5:6.5, and space velocity 15,000 $cm^3\ g^{-1}\ h^{-1}$. Results are after 2 h of reaction. Total flow = 50 ml min^{-1} (NPT).

RESULTS

Noncatalytic Reactions

The reaction involving methane, oxygen and acetonitrile vapor with helium as a diluent, i.e., the oxidative methylation of acetonitrile, was first carried out in an empty reactor (without any catalyst) both in the absence and the presence of quartz wool plugs at 650°–850°C in order to examine the contribution of the homogeneous gas-phase reaction. The results obtained at 750°C are presented in Table 2 which shows that this noncatalytic contribution is insignificant compared with the catalytic performance.

Catalytic Performances

The calcined CaO and mono- or bialkali metal compound(s) promoted CaO are low surface area (<10.0 m^2/g) crystalline materials (Table 1). Upon promoting CaO with the alkali metal sulfate(s), the surface areas of the resulting materials decreased. These decreases are more noticeable with the bialkali promoted CaO than the monoalkali promoted ones. These are consistent with our previous findings with MgO-based catalysts (19, 20).

The decreases in surface area did not decrease the catalytic performance of the alkali promoted systems. Rather the performances were much higher than with unpromoted CaO and the selectivities to the desired products increased significantly. The main products were acrylonitrile, propionitrile, C_2 hydrocarbons, hydrogen cyanide, and carbon oxides and a trace amount of unidentified compounds. The unpromoted CaO exhibited some activity with an acrylonitrile selectivity of 16.0 mol% and yield of 2.6% (Table 2). All the conversions (of CH_4, O_2 and CH_3CN) increased compared to noncatalytic systems but are much lower than those over the mono- or bialkali promoted CaO. Carbon oxides and hydrogen cyanides are the dominant products. Nevertheless, the overall increase in the acrylonitrile and propionitrile yields indicates that a substrate with basic properties, such as CaO, is beneficial for the process. This was confirmed by replacing CaO with SiO_2 (Aldrich, 600 m^2/g), which showed a negligible performance.

Monoalkali Metal Compound(s) Promoted CaO

Substantial increases in the methane, oxygen and acetonitrile conversions and the selectivity to acrylonitrile were observed upon promoting CaO with any monoalkali metal compound (from sulfate, hydroxide, chloride, acetate, carbonate or nitrate precursors), compared with the results obtained over the unpromoted CaO. The best results were, however, obtained over the catalysts prepared from the sulfate precursors and are presented in Table 2. Depending on the nature of the alkali cations and, to a smaller extent, on the nature of the associated anions, the five monoalkali promoted CaO catalysts exhibited varying performances, with the selectivity to acrylonitrile between 29.0 and 39.0 mol% and the yield between 4.9 and 8.6%. The propionitrile yield also showed some increase compared to the unpromoted CaO but much lower than that of acrylonitrile. The 10 mol% Na^+/CaO showed the highest acetonitrile conversion of 22.0 mol% and acrylonitrile selectivity of 39.0 mol%, followed closely by the 10 mol% Cs^+/CaO, whereas Rb^+/CaO was found to be the least effective catalyst, followed closely by K^-/CaO. Although the Li^+/CaO system showed good performances initially, it became almost inactive gradually due, presumably, to the volatility of Li (23).

In general, in terms of the acrylonitrile yield, the following sequence for the alkali cations was observed: $Na^+ > Cs^+ > Li^+ > K^+ > Rb^+$. A similar sequence was observed in the oxidative methylation of toluene to styrene (20). The influence of the anions was less prominent and the differences among them were quite small.

Bialkali Metal Compound(s) Promoted CaO

Significant increases in the conversion of acetonitrile, particularly in the selectivity to acrylonitrile, and substantial increases in methane conversion were observed upon promoting CaO with any bialkali metal compound, such as Li*A* + Na*A*, Li*A* + Cs*A*, Na*A* + Cs*A*, or K*A* + Cs*A* ($A = SO_4^{2-}$, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-), compared to those over the respective monoalkali promoted CaO. The results obtained over CaO-supported 10 different bialkalis derived from the SO_4^{2-} precursors are presented in Table 2. The acetonitrile conversion increased up to 36.0 mol%, the methane conversion up to 12.0 mol% and O_2 up to 96.0 mol%. The selectivity to acrylonitrile noticeably increased up to 70.0 mol% and that to propionitrile also increased to some extent. As a result, the acrylonitrile yield became as high as 25.2%. This is one of the highest yields ever reported. The selectivities to carbon oxides and hydrogen cyanide decreased drastically.

The catalytic performances, however, depend on the nature of the alkali compounds forming the pair, the reaction conditions and to a smaller extent on the nature of the anion. Thus, the maximum steady-state methane and acetonitrile conversions and the highest selectivity (70 mol%) to acrylonitrile were obtained over (5 mol% Na^+ + 5 mol% Cs^+)/CaO (prepared from the sulfate precursors). This gave rise to an acrylonitrile yield of 25.2%, which is much higher than those over any monoalkali promoted CaO. The propionitrile yield was only 3.2%, which is slightly higher than those over the monoalkali promoted systems. Other bialkali promoted CaO (e.g., K*A* + Cs*A*, Li*A* + Cs*A*, or Li*A* + Cs*A*, where $A = SO_4^{2-}$, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-) also showed noticeable increases in the acrylonitrile yield, the propionitrile yield remaining nearly the same as for the monoalkali promoted CaO. The least effective among the bialkali systems was (5 mol% K^+ + 5 mol% Rb^+)/CaO with an acetonitrile conversion of 27.0 mol% and an acrylonitrile selectivity of 54.0 mol%. These values are still much higher than those obtained over any monoalkali promoted CaO. In terms of the influence of the anions, SO_4^{2-} was found to be the most effective followed closely by other anions. It should be noted that the effect of the nature of the bialkali cations was much more pronounced than that of the anions. The effect of bialkali metal loading on the performance of the resulting catalyst indicated that the total alkali loading of 10 mol% with an equal molar amount of both the alkalis was the most effective. A further increase in the total alkali loading did not increase the performance.

Effects of Reaction Temperature and Stability with Time-on-Stream

Further studies regarding the effects of the operating conditions focused on $Na^+ + Cs^+$, $K^+ + Cs^+$, or $Na^+ + K^+$ (from the sulfate precursors) supported on CaO and the respective monoalkali promoted systems.

The selectivity to acrylonitrile increased with the increase in temperature passing through a maximum at 750°C for both the mono- and bialkali promoted systems (Fig. 2a). The decrease in selectivity after 750°C was more pronounced over monoalkali promoted systems than the bialkali ones. The latter systems also have higher initial values than the former. The best selectivity (70.0 mol%) was exhibited by (5% Na^+ + 5% Cs^+)/CaO at 750°C followed by a slow decrease. The acrylonitrile yield, continued to increase, however, with the increase in temperature up to 850°C over the bialkali promoted systems, unlike the monoalkali ones (Fig. 2b). This occurs because the acetonitrile conversion increased with the temperature over the former systems, resulting in an acrylonitrile yield as high as 29.4% at 850°C over ($Na^+ + Cs^+$)/CaO.

A major difference between the mono- and the bialkali metal compound promoted CaO systems was observed with time-on-stream. The stability with time-on-stream of the bialkali promoted systems (measured as the change in acrylonitrile selectivity and yield) is much higher than that of the monoalkali promoted systems (Figs. 3a and 3b). Thus, during 60 h of operation the acrylonitrile selectivities over the monoalkali promoted systems suffered a 55–60% decrease compared to the initial values, the 10 mol% Cs^+/CaO being the least stable one (Fig. 3a). In contrast, the selectivities over the bialkali promoted systems, after an initial increase, remained almost unchanged (only a variation of 5–7% was observed). The acetonitrile conversions also suffered noticeable decreases (by 45–50%) over the monoalkali promoted systems, unlike the bialkali promoted ones, which showed only a small

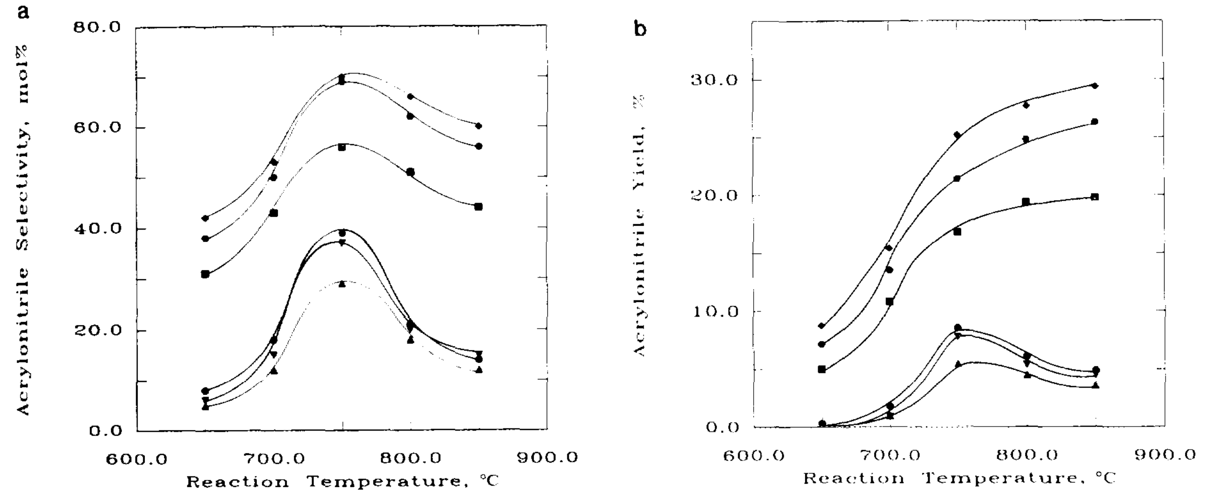


FIG. 2. Effects of reaction temperatures on the acrylonitrile selectivity (a) and yield (b) over mono- and bialkali metal sulfate(s) promoted CaO. Reaction conditions: temperature 750°C, pressure 1 atm, $P(CH_4):P(O_2):P(CH_3CN):P(He) = 5.0:1.0:1.5:6.5$ and space velocity 15,000 $cm^3g^{-1}h^{-1}$. The products were measured after 2 h of reaction: ●, 10 mol% Na^+/CaO; ▲, 10 mol% K^+/CaO; ▼, 10 mol% Cs^+/CaO; ■, (5 mol% Na^+ + 5 mol% K^+)/CaO; ◆, (5 mol% Na^+ + 5 mol% Cs^+)/CaO; ⬢, (5 mol% K^+ + 5 mol% Cs^+)/CaO.

decrease (by 7–10%, not shown in the figure). As a result, much higher and stable acrylonitrile yields were obtained over the bialkali promoted systems than over the monoalkali promoted systems, the (Na^+ + Cs^+)/CaO system being the most stable one.

Effects of the Pseudocontact Time

In order to determine the effects of the pseudocontact time (or the reciprocal space velocity W/F), the amount of catalyst (W) was varied while holding the flow rate (F) constant. Figures 4a and 4b show the effect of the pseudocontact time on the acrylonitrile selectivity and yield. For both the monoalkali and the bialkali promoted systems, the acrylonitrile selectivity first increases with the increase in the pseudo-contact time, passes through a maximum at $W/F = 0.24$ g · s/ml (Fig. 4a) followed by some decrease. The decrease is, however, much smaller over the bialkali promoted systems. At longer contact times the selectivity to carbon oxides increases over all the systems. The acrylonitrile yield increases continuously over the bialkali promoted systems, whereas those over the monoalkali promoted systems pass through a maximum at $W/F = 0.24$ g · s/ml (Fig. 4b). This happens due to the increase in the acetonitrile conversion with the pseudocontact time over both the systems and the different extents of decrease of the selectivity.

Effect of the Partial Pressures of the Reactants

The effect of methane partial pressure on the acrylonitrile selectivity and yield, at constant partial pressures of acetonitrile and oxygen and other reaction conditions (with the exception of the partial pressure of He) fixed, are presented in Figs. 5a and 5b. The differences between the mono- and bialkali promoted systems are quite noticeable. For the former systems, the acrylonitrile selectivity passes through maxima at $P(CH_4) = 271$ Torr followed by noticeable decreases (Fig. 5a). For the bialkali promoted systems, the acrylonitrile selectivity increases with increasing partial pressure, the increase being more prominent up to $P(CH_4) = 271$ Torr, followed by an almost constant value. This gives rise to much higher acrylonitrile yields for the bialkali promoted systems than the monoalkali ones (Fig. 5b). An acrylonitrile yield as high as 30.2% was obtained over (5% Na^+ + 5% Cs^+)/CaO at $P(CH_4) = 600$ Torr. This is due to the increase in both the acetonitrile conversion and the acrylonitrile selectivity.

Figures 6a and 6b demonstrate the effect of the partial pressure of acetonitrile on the acrylonitrile selectivity and yield, while keeping the partial pressures of methane and oxygen and other reaction conditions (with the exception of the partial pressure of He) constant. As before, a noticeable difference between the mono- and bialkali promoted systems is observed. The acrylonitrile selectivity increases initially with increasing partial pressure of acetonitrile over both the systems up to $P(CH_3CN) = 81$ Torr (Fig. 6a), the increases being, however, more prominent for the bialkali systems, followed by some decrease. The acetonitrile conversion also increased over both the systems (not shown). As a result, the acrylonitrile yield increased over all the catalysts. Nevertheless, the bialkali promoted systems exhibited much higher yields (Fig. 6b) than the monoalkali promoted ones, the (5% Na^+ + 5% Cs^+)/CaO exhibiting the highest yield (30.3%) at $P(CH_3CN) = 120$ Torr.

The effect of the partial pressure of oxygen on the

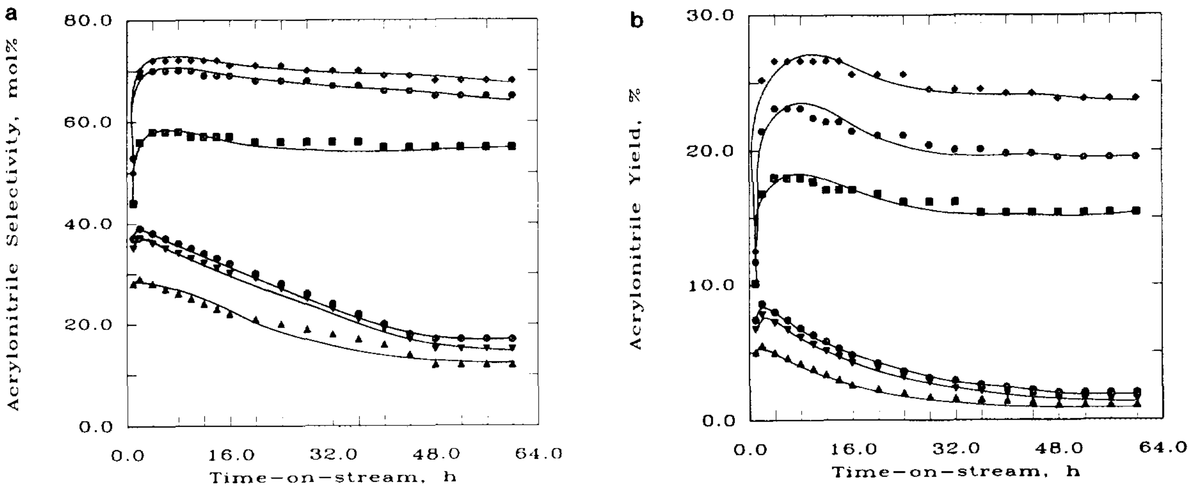


FIG. 3. Change in the acrylonitrile selectivity (a) and yield (b) over mono- and bialkali metal sulfate promoted CaO. The reaction conditions and the symbols are as in Fig. 2.

acrylonitrile selectivity and yield is presented in Figs. 7a and 7b, while keeping the partial pressures of methane and acetonitrile and the other reaction conditions (with the exception of the partial pressure of He) constant. With the increase in partial pressure of oxygen, the acrylonitrile selectivity passes through maxima at $P(O_2)$ = 54 Torr over both the systems (Fig. 7a). The acetonitrile conversion increases, however, with increasing partial pressure of oxygen, the increase being more prominent for the bialkali promoted systems. As a result, the acrylonitrile yield increases over the bialkali promoted systems, giving a yield of 26.2% at $P(O_2)$ = 120 Torr (Fig. 7b). In contrast, the acrylonitrile yield slowly decreases starting from $P(O_2)$ = 54 Torr over the monoalkali promoted systems.

Basicity and Base Strength Distribution

The basicity and base strength of unpromoted CaO and mono- or bialkali metal sulfate promoted CaO (calcined in situ in helium flow at 850°C, 15 h) were determined by the STD method and by the benzoic acid titration. We present, however, only the results based on the latter method because it can clearly identify the systems which possess sites with superbasic strength. Table 3 presents the concentration of basic ionic sites of the CaO-supported samples. It can be seen that only the three bialkali promoted CaO systems have an appreciable basicity in the superbasic range $26.0 \leq H_-$. In contrast, pure CaO or the monoalkali promoted CaO systems do not show

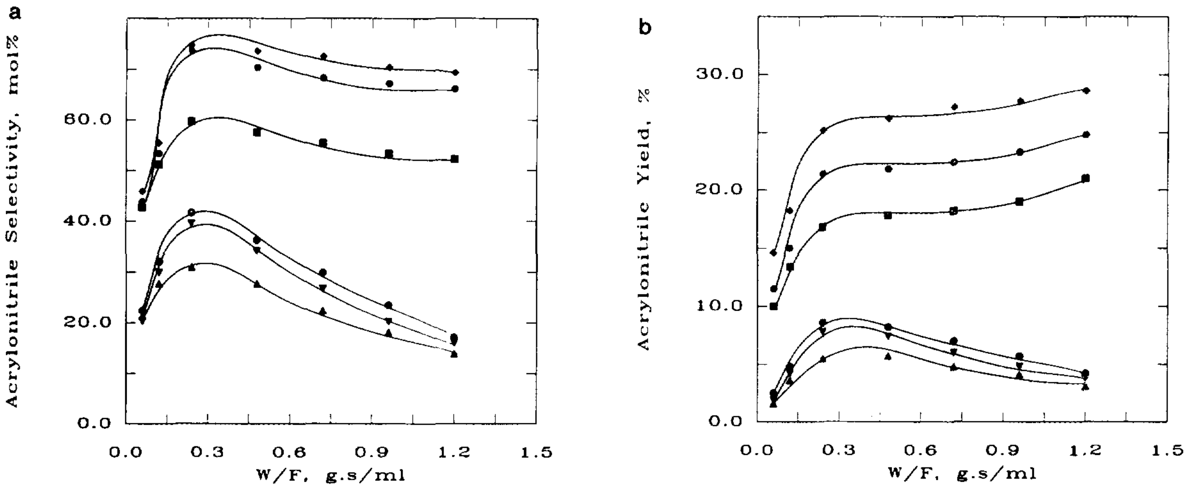


FIG. 4. Effect of pseudocontact time (*W*/*F*) on the acrylonitrile selectivity (a) and yield (b) over mono- and bialkali metal sulfate promoted CaO. The reaction conditions and the symbols are as in Fig. 2, except for the space velocity.

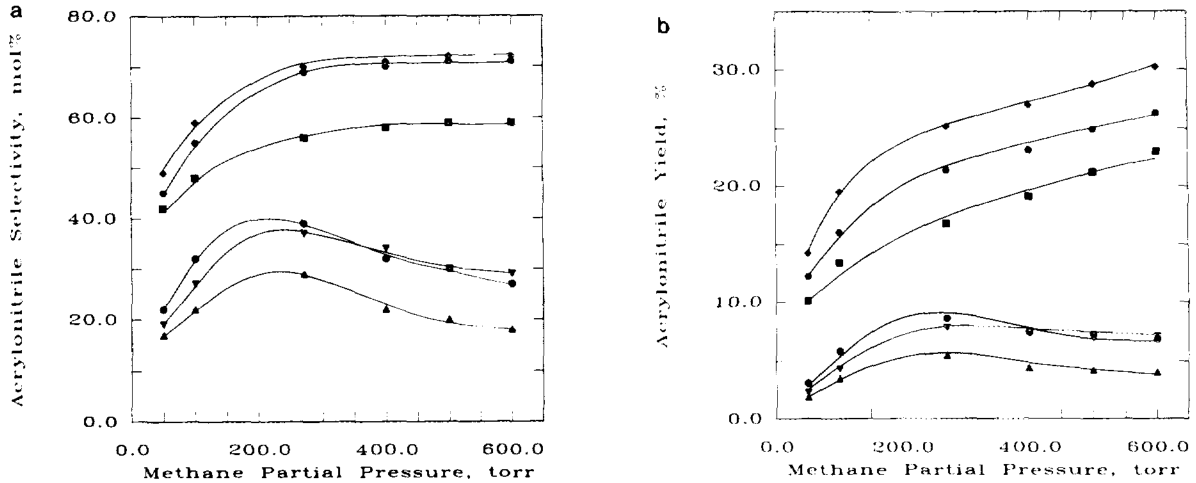


FIG. 5. Effect of methane partial pressure in the feed gas on the acrylonitrile selectivity (a) and yield (b) over mono- and bialkali metal sulfate promoted CaO. The reaction conditions and the symbols are as in Fig. 2, except for the methane partial pressure.

any basicity in the superbasic range, although they show good basicity in the other range.

This method is quite accurate as concerns the strength of the basic sites since the strength is based on a logarithmic scale. It is, however, less accurate regarding the number of sites in the various strength intervals. Significant in the present context is, however, the fact that the method can clearly identify sites of superbasic strength.

DISCUSSION

Catalytic Performance

The present results demonstrate that upon promoting CaO with bialkali metal compounds, more active, selective and stable with time-on-stream catalysts than any monoalkali compound promoted CaO or unpromoted CaO are obtained in the oxidative methylation of acetonitrile with methane to acrylonitrile. Depending upon the nature of the promoter compounds forming the pair, the concentrations of the alkali ions and the reaction conditions, a noticeable improvement in the acrylonitrile selectivity and yield is obtained, which remains almost unchanged for a period of 60 h. The most effective catalytic systems were obtained with the bialkali metal compounds of Na*A* + Cs*A*, K*A* + Cs*A*, or Li*A* + Cs*A* (A = SO_4^{2-}, OH^-, Cl^-, CH_3COO^-, CO_3^{2-}, or NO_3^-) that contain an appropriate alkali loading (total of 10 mol%), the latter system (Li*A* + Cs*A*) being less stable than the others. The nature of the cations forming the pair exerts a much

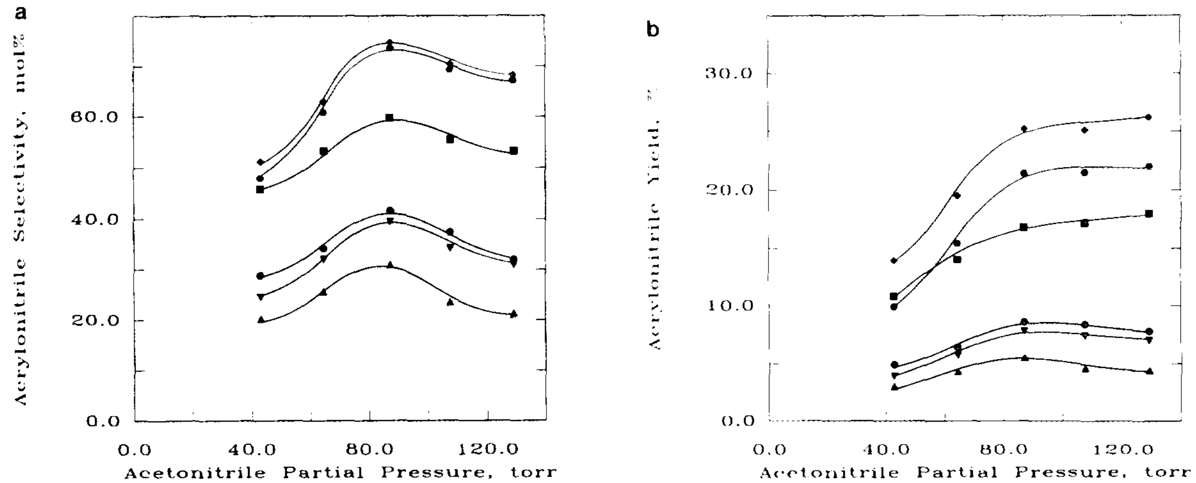


FIG. 6. Effect of acetonitrile partial pressure in the feed gas on the acrylonitrile selectivity (a) and yield (b) over mono- and bialkali metal sulfate promoted CaO. The reaction conditions and the symbols are as in Fig. 2, except for the acetonitrile partial pressure.

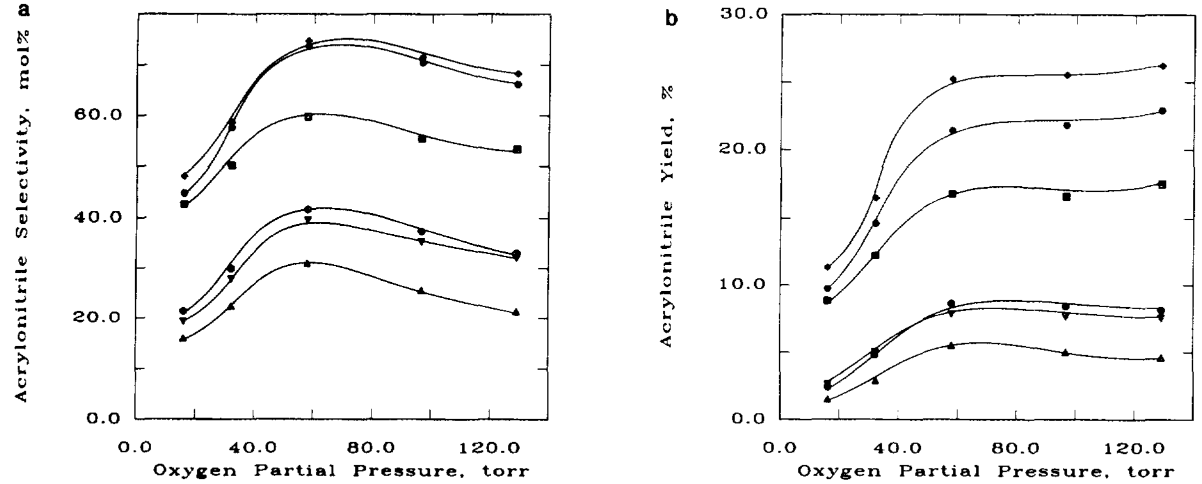


FIG. 7. Effect of oxygen partial pressure in the feed gas on the acrylonitrile selectivity (a) and yield (b) over mono- and bialkali metal sulfate promoted CaO. The reaction conditions and the symbols are as in Fig. 2, except for the oxygen partial pressure.

stronger influence on the catalyst performance than that of the anion, as evidenced by the small changes in performance among the anions. In fact, after calcination, all the alkali compounds promoted MgO are converted into the corresponding alkali oxides, as evidenced by the absence of even traces of chlorine, sulfur or nitrogen in the samples investigated by XPS (20). It is the extent of surface O^{2-} due to basicity (as discussed later) that plays a crucial role.

TABLE 3

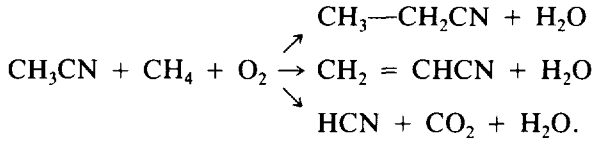
Concentration of Basic Ionic Sites on the Surface of CaO and Mono- or Bialkali Metal Sulfate Promoted CaO as Measured by the Benzoic Acid Titration Method[a]

Sample (alkali loading in mol%)	Concentration of basic ionic sites (mmol/g)	
	$12.2 \leq H_-$[b]	$26.5 \leq H_-$
CaO	0.11	0.00
10% Li^+/CaO	0.18	0.00
10% Na^+/CaO	0.19	0.00
10% K^+/CaO	0.14	0.00
10% Cs^+/CaO	0.17	0.00
(5% Li^+ + 5% Cs^+)/CaO	0.24	0.13
(5% Na^+ + 5% Cs^+)/CaO	0.23	0.16
(5% K^+ + 5% Cs^+)/CaO	0.21	0.14

[a] All samples were calcined at 750°C for 15 h.

[b] H_- is the base strength determined from the pK value of an adsorbed indicator according to $H_- = pK_a + \log [B^-]/[BH]$, where p$K_a$ is the negative logarithm of the dissociation constant of the indicator, [BH] is the concentration of the acidic form of the indicator, and $[B^-]$ is the concentration of the basic form; the $[B^-]/[BH]$ ratio is considered to be 1.

The oxidative methylation of acetonitrile yields in addition to acrylonitrile and propionitrile also hydrogen cyanide and carbon oxides. The reactions can be represented as



$$CH_3CN + CH_4 + O_2 \rightarrow \begin{cases} \nearrow CH_3{-}CH_2CN + H_2O \\ \rightarrow CH_2 = CHCN + H_2O \\ \searrow HCN + CO_2 + H_2O. \end{cases}$$

The promoter effects of Na*A* + Cs*A*, K*A* + Cs*A*, or Li*A* + Cs*A* are synergistic, since individually none of these alkali promoted CaO exhibits such high performances. A similar observation was made by us previously with the CaO- or MgO-supported systems in the oxidative methylation of toluene (20, 21). The difference in performances is clearly not directly dependent on the specific surface area, because the bialkali promoted CaO systems have the lowest surface area (3–4 m^2/g) (Table 1). Replacing CaO with a high surface area SiO_2 (600 m^2/g) in the mono- or bialkali promoted systems resulted in ineffective catalysts. A high surface area may promote advanced oxidation, and hence a lower acrylonitrile yield. Even the best catalyst (KBr/SiO_2) reported in Ref. (9) failed to exhibit any promising results in the present study. This indicates that the substrate with basic properties (CaO) and relatively small specific surface area, when promoted with the bialkali metal compounds produces effective systems (the effect of basicity is discussed later).

Effects of the Operating Conditions

As in our previous studies for different reactions (19–21), in the present study the best performances are also exhibited by the bialkali promoted systems containing a total alkali loading of 10 mol% (5 mol% each). The striking differences between the mono- and bialkali promoted CaO is not due to the loading, since the monoalkali promoted CaO failed to show any comparable performance even at the higher alkali loading of 20.0 mol%. (In fact, the performance was lower at 20 mol% than that at 10 mol%.)

The effect of the operating conditions (reaction temperature, pseudo-contact time, stability with time-on-stream and partial pressures of the reactants) on the performance of the catalysts could determine not only the optimum conditions for obtaining the highest acrylonitrile yield but also could shed some light on the possible routes for the product formations. The observations that the acrylonitrile selectivity increases in the presence of methane and that in the absence of methane in the feed stream a small amount of acrylonitrile is still obtained suggests that two parallel reactions may occur over the catalyst surface: (a) the oxidative methylation of acetonitrile to propionitrile, followed by its oxidative dehydrogenation to acrylonitrile; and, to a smaller extent, (b) the oxidative disproportionation of acetonitrile to acrylonitrile and hydrogen cyanide. A similar observation was made in Refs. (6, 9).

The intermediates for the oxidative methylation of acetonitrile with methane were hypothesized to be the radicals $\dot{C}H_3$, $\dot{C}H_2CN$, $H\dot{O}_2$ (9). The methyl and acetonitrile radicals are formed by the abstraction of hydrogens from methane and acetonitrile, respectively. The cross-coupling of these two radicals may be responsible for the formation of propionitrile via a new C–C bond formation

$$\dot{C}H_3 + \dot{C}H_2CN \rightarrow CH_3CH_2CN$$

followed by its dehydrogenation to acrylonitrile.

Another possibility, suggested by Khcheyan *et al.* (9), is that propionitrile is produced via the direct reaction of the methyl radical with acetonitrile. Propionitrile is oxidatively dehydrogenated to acrylonitrile with the formation of a C=C bond:

$$\begin{gathered} CH_4 + O_2 \rightarrow \dot{C}H_3 + HO_2^{\cdot} \\ CH_4 + H\dot{O}_2 \rightarrow \dot{C}H_3 + 2HO^{\cdot} \\ CH_4 + H\dot{O} \rightarrow \dot{C}H_3 + H_2O \\ \dot{C}H_3 + CH_3CN \rightarrow CH_3CH_2CN + H^{\cdot} \\ CH_3CH_2CN + O_2 \rightarrow CH_2 = CHCN + 2HO^{\cdot} \\ CH_4 + H^{\cdot} \rightarrow \dot{C}H_3 + H_2. \end{gathered}$$

Figure 2 indicates that even at the low temperature of 650°C, a fairly good acrylonitrile selectivity (31–42 mol%) and acetonitrile conversion (16–21 mol%) are obtained over the bialkali promoted CaO. In contrast, the monoalkali promoted ones lead to some dark tary products in addition to much smaller yields of acrylonitrile (5–8 mol%). This is perhaps because even at such a low temperature both the methyl and acetonitrile radicals are readily formed over the surface of bialkali promoted catalysts and their cross-coupling leads to acrylonitrile. The dark products formed with the monoalkali promoted systems suggest that in such systems a radical polymerization takes place because few CH_3 radicals are present for coupling to acetonitrile radicals. The observation that with the increase in temperature the acrylonitrile selectivity passes through a maximum over all the systems, followed by a lower decrease over the bialkali systems indicates that at higher temperatures (>750°C) the cross-coupling of the radicals is increasingly replaced by the oxidation to carbon oxides and water and the formation of hydrogen cyanide. The acrylonitrile yield continues to increase with temperature over the bialkali promoted systems because the appreciable rise in conversion is accompanied by only a moderate decrease in selectivity, unlike the situation found with the monoalkali-promoted systems.

The effect of the pseudo-contact time on the product selectivity and yield may also suggest a possible reaction path. At short contact times (<0.24 g·s/ml) a substantial amount of propionitrile was observed, particularly over the bialkali promoted systems, in addition to acrylonitrile and some undesirable products. With the increase in the pseudo-contact time, the selectivity to propionitrile decreases and that to acrylonitrile increases and passes through a maximum (Fig. 4). This indicates that propionitrile is a primary product and undergoes an easy oxidative dehydrogenation to acrylonitrile. This is consistent with Ref. (9). At longer contact times, the carbon oxides become some of the dominant products, indicating that the reactants and the products are more prone to oxidation, particularly over the monoalkali promoted systems. This implies that, although the mechanism of product formations over both kinds of systems is apparently the same, the bialkali promoted systems exhibit better performances due to a larger number of active sites on their surface, as discussed later.

A substantial induction period (of at least 2 h), particularly over the bialkali promoted systems, was needed for the attainment of a more steady-state behavior. It is possible that during this period a reconstruction of the catalyst surface takes place thereby ensuring a stable surface for at least 60 h (Fig. 3). It is also likely that the reaction environment (nature of reactants, partial pressures, etc.) facilitates the formation of the active surface during the induction period. After the reaction the all-grey catalysts became black, particularly the bialkali promoted CaO, indicating that a substantial coke deposition took place. In spite of this coke deposition, the selectivity to acrylonitrile continuously increased with time, while that to propionitrile decreased. This may suggest that coke deposition on the catalysts is beneficial for the formation of acrylonitrile from propionitrile.

Influence of the Basicity and Surface Concentration of Alkali

There is a noticeable difference between the mono- and bialkali promoted CaO or even among various bialkali promoted CaO systems. The basicity of the substrate and of the promoted materials plays an important role in the oxidative methylation of acetonitrile, as observed previously by us (19–21) for the oxidative coupling of methane and the oxidative methylation of toluene. In the present study it was found that the bialkali promoted CaO systems which exhibited good performances also possessed high basicity and this basicity was much higher for the bialkali promoted systems than the monoalkali promoted systems. Indeed, high basicity and base strength distribution were observed for a number of bialkali metal sulfate promoted CaO: (5 mol% Li^+ + 5 mol% Cs^+)/CaO, (5 mol% Na^+ + 5 mol% Cs^+)/CaO and (5 mol% K^+ + 5 mol% Cs^+)/CaO (Table 3). Because of their high basicity and basic strength, these three catalysts can be considered as superbases, unlike the monoalkali promoted systems. This is in accordance with the classification of Tanabe *et al.* (17) and is consistent with our previous findings of superbasicity with the bialkali metal chloride or hydroxide promoted MgO (19, 20).

The number of basic sites is much greater in the bialkali metal ions promoted CaO than in the monoalkali promoted CaO because of the higher concentration of the alkali on the surface for the same total molar loading. The high enrichment of the surface with the alkali ions was confirmed previously by XPS (19–21). As a result, the amount of surface lattice oxygen (O^{2-}) having nucleophilic character (29) is also larger in the bialkali promoted CaO. Such lattice oxygen (O^{2-}) sites are believed to facilitate the abstraction of hydrogen from both methane and acetonitrile.

CONCLUSION

The following conclusions can be drawn from the present study of oxidative methylation of acetonitrile with methane:

1. The oxidative methylation of acetonitrile with methane to acrylonitrile is a high temperature (>700°C) reaction and is found to be more effectively catalyzed by a new class of highly basic (superbasic) catalysts, prepared by promoting CaO with various binary alkali metal compounds than those promoted with any monoalkali metal compound.
2. The nature of the alkali compounds forming the pair, the concentration of the alkali promoters, and the reaction conditions are the key factors in determining the effectiveness of the catalytic systems that ensures the selective formation of acrylonitrile. The influence of the alkali cations forming the pair is more pronounced than that of the anions associated with the alkali cations.
3. The catalytic performances of the bialkali metal compounds promoted CaO are significantly higher than those over any monoalkali promoted CaO and their stability with time-on-stream is also prominent.
4. The synergistic increase in activity, selectivity and stability with time-on-stream observed over the bialkali promoted catalysts is attributed to the superbasicity of the resulting catalysts. The high enrichment of the catalyst surface with the alkali ions is believed to be responsible for the formation of superbasicity in the bialkali promoted systems.

REFERENCES

1. Keller, G., and Bhasin, M., *J. Catal.* **73,** 9 (1982).
2. Lunsford, J. H., *in* "Natural Gas Conversion" (A. Holmen, K. J. Jens, and S. Kolboe, Eds.), Studies in Surface Science and Catalysis, Vol. 61, p. 3. Elsevier, Amsterdam, 1991.
3. Lee, J. S., and Oyama, S. T., *Catal. Rev.-Sci. Eng.* **30,** 249 (1988).
4. Hutchings, G. L., Scurrell, M. S., and Woodhouse, J. R., *Chem. Soc. Rev.* **18,** 251 (1989).
5. Amenomiya, Y., Birss, V. I., Goledzinowski, M., Galuszka, J., and Sanger, A. R., *Catal. Rev.-Sci. Eng.* **32,** 163 (1990).
6. Khcheyan, Kh. E., Revenko, O. M., and Shatalova, A. N., *in* "Proceedings of the 11th World Petroleum Congress, 1983," p. 465 (1984).
7. "Kirk–Othmer Encyclopedia of Chemical Technology," Vol. 1, p. 352. Wiley, New York, 1991.
8. Perkowskii, J., *Prezem. Chem.* **51,** 17 (1972).
9. Khcheyan, Kh. E., Shatalova, A. N., Revenko, O. M., and Agrinskaya, L. E., *Neftckhimiya* **20,** 876 (1980).
10. Auvil, S. R., and Peugnite, Ch. R., Patent 4,272,452, U.S.A., 1982, 8H83.
11. Osada, Y., Enomoto, K., Fukushima, T., Ogasawara, S., Shikada, T., and Ikariya, T., *J. Chem. Soc. Chem. Commun.*, 1156 (1989).
12. Suzuki, T., Wada, K., and Watanabe, Y., *Ind. Eng. Chem. Res.* **30,** 1719 (1991).
13. Kim, H., Suh, H. M., and Paik, H., *Appl. Catal.* **87,** 115 (1992).
14. Otsuka, K., Hatano, M., and Amaya, T., *J. Catal.* **137,** 487 (1992).
15. Khan, A. Z., and Ruckenstein, E., *J. Chem. Soc. Chem. Commun.*, 587 (1993).
16. Malinowski, S., and Kijenskii, J., *in* "Catalysis" (C. Kemball and D. A. Dowden, Reporters), Vol. 4, p. 130. The Royal Society of Chemistry, London, 1980.
17. Tanabe, K., Misono, M., Ono, Y., and Hattori, H., *in* "New Solid Acids and Bases" (B. Delmon and J. T. Yates, Eds.), Studies in Surface Science and Catalysis, Vol. 51, p. 14. Elsevier, Amsterdam, 1989.
18. Ruckenstein, E., and Khan, A. Z., *Catal. Lett.* **18,** 27 (1993).
19. Ruckenstein, E., and Khan, A. Z., *J. Catal.* **141,** 628 (1993).
20. Khan, A. Z., and Ruckenstein, E., *J. Catal.* **143,** 1 (1993).
21. Khan, A. Z., and Ruckenstein, E., *Appl. Catal.* **102,** 233 (1993).
22. Ruckenstein, E., and Khan, A. Z., *J. Chem. Soc. Chem. Commun.*, 1290, 1993.

23. Khan, A. Z., and Ruckenstein, E., *J. Catal.* **138,** 322 (1992).
24. JCPDS Powder Diffraction File. International Centre for Diffraction Data, Swarthmore, 1988.
25. Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., and Muilenberg, G. D. (Eds.), "Handbook of X-ray Photoelectron Spectroscopy." Perkin–Elmer Corporation, Minnesota, 1978.
26. Malinowskii, S., and Szczepanska, S., *J. Catal.* **2,** 310 (1963).
27. Choudhary, V. R., and Rane, V. H., *Catal. Lett.* **4,** 101 (1990).
28. Khan, A. Z., and Ruckenstein, E., *J. Catal.* **139,** 304 (1993).
29. Baerns, M., and Ross, J. R. H., *in* "Perspectives in Catalysis" (J. M. Thomas and K. I. Zamaraev, Eds.), p. 315. Blackwell, London, 1992.