Study of Oxide-Based Catalysts for the Oxidative Transformation of Acetonitrile to Acrylonitrile with CH_4

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Various oxides and metal-supported oxides were studied for the oxidative transformation of acetonitrile to acrylonitrile with methane in the range 550 to 730°C. This reaction requires the activation of both methane and the α-carbon of the acetonitrile. Surprisingly, it was found that the effective coupling of the reactants to acrylonitrile does not occur over all the catalysts that are effective for oxidative coupling of methane reactions. Among all the catalysts tested, only Li/MgO with nominal composition of lithium in the range 15 to 30 wt% was effective in forming acrylonitrile. This was probably due to the maximum concentration of $[Li^+ O^-]$ surface centers which catalyze the abstraction of hydrogen from the reactants and simultaneously disfavor the undesired oxidation of the nitriles. It was concluded that the efficiency of Li/MgO could not be attributed to its basicity characteristics. Other oxides such as Sm_2O_3, La_2O_3, Bi_2O_3, and CaO either individually or loaded with monometallic and/or bimetallic combinations of alkali metals are not effective catalysts and oxidize acetonitrile to CO and CO_2. Individual magnesia and MgO-loaded with alkali metals (other than lithium) are not effective for the coupling of methane and acetonitrile to form acrylonitrile and propionitrile. We also found that the decrease in the acrylonitrile selectivity for extented periods of operation is associated with the loss of lithium from the Li/MgO catalysts. Undoped samaria and lanthana at elevated temperatures ($>680°C$) oxidize acetonitrile completely to CO and CO_2. For the latter oxides, if the oxygen fed into the reactor is the limiting reactant, then lattice oxygen is used for the complete oxidation of acetonitrile. The loading of samaria or lanthana with an alkali metal decreases the extent of oxidation reactions. This behavior is inversed when CaO is used as support. FT-IR and temperature-programmed desorption experiments indicate that the increase in the number and strength of the basic sites of the catalysts plays a negative role in the coupling of methane and acetonitrile to acrylonitrile. © 1999 Academic Press

Key Words: acetonitrile; acrylonitrile; oxidative methylation; Li/MgO.

INTRODUCTION

Nitriles, ethers, and esters with one unsaturated bond at the α- or β-position are very important feed chemicals for many industrial processes. Acrylonitrile is a typical example of a synthesis chemical that can be used as a basic chemical for the production of a large variety of everyday products. The production of acrylonitrile is based on the ammoxidation of propene which was developed in the early 1950s (SOHIO process). The reaction is carried out over multicomponent bismuth phosphomolybdate-based catalysts (1, 2). Today more than 95% of the world's acrylonitrile is produced using the Sohio ammoxidation process by BP or under its license. The main by-product during the production of acrylonitrile is acetonitrile. Although acetonitrile can undergo typical nitrile reactions leading to amines, amides, halogenated nitriles, ketones, and other chemicals (3), it finds a limited number of applications. It is used mainly as a solvent or it is incinerated since the world's acetonitrile supply is far exceeded by the demand.

Other researchers have studied the catalytic transformation of acetonitrile to the more valuable acrylonitrile by adding a carbon atom at the α-position of the former nitrile. This methylation can be achieved over basic catalysts since acetonitrile (CH_3–CN) possesses an electron-withdrawing functional group (–CN), and therefore the methyl group of acetonitrile acquires a positive charge. Methanol and formaldehyde have been used as methylating agents in this reaction. The production of acrylonitrile from the methylation of acetonitrile with methanol was carried out over alkali metals supported on silica gel (4). The performance of the catalyst increased in the order Li > Na > K > Rb but the yield of acrylonitrile remained very low. Li, Ca, or Ba phosphates on silica (5) and K, Cs, or Zr supported on silica catalysts (6) were used as well. Higher yields of acrylonitrile, namely, up to 80% based on the formaldehyde supplied, were observed over the former type of catalyst at approximately 400°C. MgO loaded with metals such as Cr, Fe, Mn, and Cu was found to selectively transform methanol and acetonitrile to acrylonitrile at temperatures in the range 350 to 400°C (7–10). However, under those conditions, the maximum conversion of acetonitrile was about 10%. It was found that the rate-limiting step was the abstraction of the proton from the methyl group of acetonitrile occurring over the basic sites. Similar results were observed by others (11)

over silica gel-supported catalysts containing oxides of Bi, Sb, Mo, or Fe. Methane has been used as a methylating agent during the oxidative transformation of acetonitrile to acrylonitrile at relatively high temperatures. Khcheyan and his co-workers studied this reaction over Sb_2O_3, MoO_2, and BiO_2 oxides supported with K or Ca (12, 13) and over KBr on quartz (14, 15). It was found that this reaction can take place, thus indicating that the methane can be activated over those catalysts. Thermodynamic analysis (12) showed that acrylonitrile can be formed from the reaction of methane with acetonitrile only in the presence of oxygen in the range 300 to $1000°C$. Other researchers (16) studied the catalytic performance of CaO loaded with bimetallic combinations of alkali metals. Those catalysts were effective for the methylation of acetonitrile to acrylonitrile. Even though methane is readily available and cheaper than other organics with one carbon atom, such as methanol and formaldehyde, methane is a very stable molecule and, therefore, its activation is not an easy task. For this reason, relatively high temperature is required to activate methane and assist the cleavage of the C–H bond. However, at high temperatures acetonitrile is more readily oxidized to CO and CO_2.

In this paper we study the performance of oxide-based catalysts for the oxidative methylation of acetonitrile to acrylonitrile with CH_4 at temperatures ranging from 550 to $730°C$. We found that the majority of the catalysts that are effective for the oxidative coupling of methane to hydrocarbons do not favor the oxidative methylation of acetonitrile to acrylonitrile. MgO loaded with lithium was the most active and selective catalysts for this reaction.

EXPERIMENTAL

Catalyst Synthesis

The mono- and bimetallic catalysts used in this study were synthesized by mixing the corresponding oxide with the appropriate concentration of the metal precursor. High-purity oxides (MgO, 98%; La_2O_3, 99.99%; Sm_2O_3, 99.99%; Bi_2O_3 99.99%) were purchased from Aldrich Chemical Company. A known weight (2 g) of the oxide (on dry basis), distilled water (80 ml), and the necessary amount of the metal precursor(s) were heated ($95°C$) and mixed vigorously until the water evaporated completely (about 2 h). The nominal composition of the catalysts synthesized is given in the Table 1. The precursors used (M_xCl_y, where $M = Na$, K, Rb, Cs, Y, Sm, and La) were acquired from Aldrich Chemical Company. LiCl was purchased from Fischer Scientific. The catalyst was ground and then calcined in dry air at $700°C$ for 14 h. Large volumes of gases evolved during the calcination due to the decomposition of the chloride precursors. A second grinding of the calcined catalysts was performed. The catalysts used in this study (Table 1) were stored in a

TABLE 1

Properties of Oxides and Oxide-Based Catalysts Studied for the Methylation of Acetonitrile to Acrylonitrile with Methane

| Catalyst | Nominal loading of metal(s) (wt%)[a] | | BET surface area[b] (m^2/g) | Concentration of metal(s) after calcination (wt%)[c] | |
	First metal	Second metal		First metal	Second metal
MgO	—	—	7.7	—	—
Sm_2O_3	—	—	2.4	—	—
La_2O_3	—	—	0.3	—	—
Li/Sm_2O_3	10.0 & 20.0		0.3 & 0.8	0.21 & 0.22	—
Li/La_2O_3	20	—	0.7	0.1	—
Li/MgO	20	—	2.1	8.0	—
Na/MgO	20	—	5.4	13.3	—
K/MgO	20	—	7.8	10.4	—
Bi_2O_3	—	—	2.2	—	—
Y_2O_3/Bi_2O_3	—	—	5.0	—	—
CaO	—	—	0.3	—	—
Na/CaO	5.5	—	0.4	3.7	—
Cs/Na/CaO	5.5	5.5	2.9	0.5	2.1
Cs/K/CaO	5.3	5.3	3.5	0.08	0.8
Li/La/MgO	22	11	0.4	7.5	6.0
Li/Sm/MgO	24	12	0.6	7.3	7.7
Li/Cs/MgO	21	10.5	0.7	6.8	4.5
Li/Pr/MgO	22	11	0.8	6.0	4.5

Note. The chemical composition of cesium and potassium were determined by Galbraith Labs.

[a] For determination of the nominal concentration of the metal(s) loaded on the support (dry basis) the chloride was not included in the estimation.

[b] The BET surface area was measured on a dry basis after the calcination step.

[c] The calcination step was carried out at $700°C$ for 14 h in air. The concentration(s) of metal(s) reported in this table are determined by including the chloride atoms of each sample.

vacuum drier at $120°C$ to prevent the adsorption of water and CO_2.

Characterization of the Catalysts

The basicity and the strength distribution of the basic sites of selected catalysts were determined with CO_2 temperature-programmed desorption experiments (TPD). For each experiment 50 ± 2 mg of catalyst (on dry basis) were loaded between two quartz wool plugs located in the middle of an alumina tube (o.d. $\frac{1}{4}$ in.). The tube was placed inside a tubular furnace and the temperature of the bed was controlled and programmed by an OMEGA temperature controller. The exit of the bed was connected with a thermal conductivity detector for on-line detection of the CO_2 desorbed from the catalyst and any temperature. The catalyst was initially cleaned by purging high-purity He ($<99.999\%$) at $450°C$ for 1 h. The temperature of the bed was decreased to $150°C$ in helium where the CO_2 chemisorption took place. Carbon dioxide (4% in helium) was admitted to the bed until complete saturation of all the basic sites was achieved. After this step, the catalyst

was purged with helium (30 cm^3/min) for more than 5 h to remove any physisorbed carbon dioxide. The temperature was then raised to 800°C at 5°C/min. The flow rate of helium was maintained throughout the remainder of the experiment at 30 cm^3/min. For the TGA experiments 20 mg of catalyst was loaded onto the pan. All other procedures were the same as the regular TPD tests. For the FT-IR experiments self-supported wafers ($\approx$10 mg, $\frac{3}{8}$ in. in diameter) of the catalyst were made. The samples were placed in a high-vacuum bakable infrared cell equipped with CaF$_2$ windows. The spectra were recorded with a Bio-Rad FTS-40 Fourier transformed infrared spectrophotometer at a resolution of 2 cm^{-1}. The samples were cleaned *in situ* by purging with helium at 550°C. The wafer was cooled down at 150°C and CO$_2$ was admitted into the cell. Subsequently, helium was supplied to the cell (kept at 150°C) for sufficient time to remove any physisorbed CO$_2$. The temperature of the wafers was raised gradually to different temperatures in the range 150 to 550°C. All the IR spectra were normalized based on the weight of the wafer to allow comparisons. The catalysts employed in the present work were tested for superbasicity by the means of titrations as well. Details for this method which is based on indicators with different pK_a values are presented elsewhere (17).

The surface area of the catalysts was determined with a BET apparatus (Micromeritics Gemini 2320). The samples were dried at 110°C overnight prior to the BET surface area analyses. The composition of metal(s) on the supports after the initial calcination step and/or after reaction was determined with ICP spectroscopy. A known amount of powder (on dry basis) was dissolved in a 2% HNO$_3$ solution.

Catalytic Experiments

The catalytic experiments were performed in a differential plug flow reactor. For the majority of the experiments unless otherwise specified, 100 $\pm$ 2 mg (on dry basis) of fresh catalyst was loaded between two plugs of quartz wool located in the middle of an alumina tube (o.d. $= \frac{1}{4}$ in. i.d. $= \frac{5}{32}$ in.). The tube was placed horizontally inside a tubular temperature-programmable furnace (Lindberg). The gases used in this study were supplied to the reactor by four separate stainless-steel lines. The gases used were methane (Matheson, 4.21% in helium), oxygen (Matheson, 4.28% in helium), and high-purity helium (Wright Bros, 99.995%) for balance. The flow rates of the gases fed to the reactor were controlled very accurately by means of four anticorrosive mass flow controllers (MKS Instruments, Inc.). The flow rate of each gas was adjusted accordingly to achieve the required composition. Acetonitrile (Fisher, 99.9%) was introduced into the reactor at the appropriate flow rate with a liquid infusion pump through a heated line ($T \geq 130°C$). For a typical catalytic experiment the temperature of the catalyst was raised at a rate of 15°C/min to 450°C. The oxygen mixture was passed through the bed for

1 h and then the temperature was raised to the reaction temperature with the above heating rate.

The on-line analyses of the reactor effluent were carried out with a gas chromatograph (Hewlett–Packard, 5890 Series II) equipped with a mass spectrometer (Hewlett–Packard, 5792 Series II). The reactor effluent stream was sent directly to the GC through a heated line (160°C). The GC was loaded with three columns in series, namely, (1) a fused-silica PoraPLOT capillary column (0.53-mm i.d., 28-m long, with a film thickness of 20 μm), (2) a Supelco Carboxen 1000 column (stainless steel $\frac{1}{8}$ in., 15 ft long), and (3) a high-performance capillary column (HP-5, crosslinked 5%) phenylmethylsiloxane, 0.32-mm i.d., 30 m long, and a film thickness of 0.25 μm). This column configuration in conjunction with the mass spectrometer allowed the effective separation and quantitative identification of all the products of the reaction. For the quantitiative analyses calibrations with known quantities of the reactants and of each chemical species identified as products were carried out. The GC/MS unit was connected with a PC unit for data acquisition and storage.

RESULTS AND DISCUSSION

For the selective transformation of acetonitrile to acrylonitrile a carbon atom must be added to the carbon located at the α-position of the cyanide group. Since acetonitrile possesses an electron-withdrawing species (–CN), the methyl group of acetonitrile acquires a positive charge and, therefore, it can be attracted by basic sites. A successful catalyst for the production of acrylonitrile should be able to activate methane as well. Hence, catalysts that favor the oxidative coupling of methane (OCM) can in principle catalyze the above reaction. This is because OCM catalysts can form methyl radicals from methane (18, 19) and simultaneously activate the methyl group of acetonitrile at the basic sites.

In the present study we investigate the performance of selected oxides and oxide-based catalysts for the high-temperature transformation of methane and acetonitrile to acrylonitrile in the presence of oxygen according to the following general reaction. Alkali metals and selected metals from the group of lanthanides, namely, Pr, La, and Sm, were used as dopants to synthesize the mono- and bimetallic catalysts:

$$CH_3CN + CH_4 + O_2 \rightarrow CH_2{=}CHCN + 2H_2O. \quad [1]$$

Sm$_2$O$_3$

Samaria was tested because earlier investigations (20–22) showed that it is an active and selective catalyst for production of C$_{2+}$ hydrocarbons during OCM reactions. It was proposed (22) that the [Sm^{3+}O$^-$] species were formed on the surface of Sm$_2$O$_3$. The conversion of acetonitrile increases slowly for temperatures below about 640°C, but
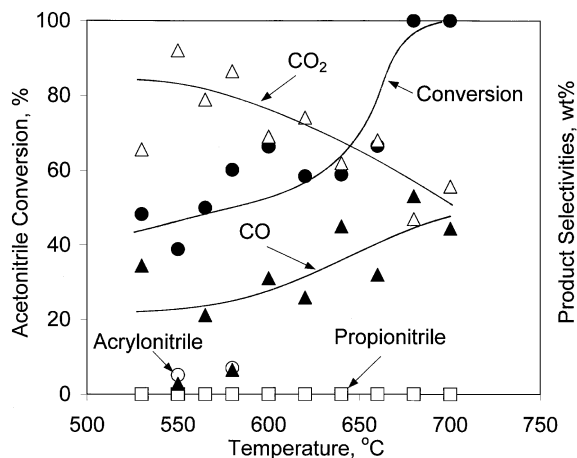
FIG. 1. Acetonitrile conversion and selectivities of CO, CO$_2$, acrylonitrile, and propionitrile over Sm$_2$O$_3$ versus reaction temperature [WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH$_4$/acetonitrile/O$_2$ = 5/2/1 (molar), 1 h on stream].

for higher temperatures it increases abruptly, reaching complete conversion (Fig. 1). The following figures show the selectivities of products containing carbon (exclude nitrogen selectivity). The molar ratio of acetonitrile to O$_2$ (limiting reactant) was 2/1. This was decided to provide the necessary oxygen for the methylation of acetonitrile to acrylonitrile and simultaneously keep the undesired oxidation reactions at relatively low levels. However, the complete conversion of acetonitrile at temperatures above about 670°C to CO and CO$_2$ cannot be justified based on the oxygen fed into the reactor. The complete transformation of acetonitrile to CO$_x$ at high temperatures when the feed stream is lacking oxygen can be explained by the utilization of lattice oxygen. From the time-on-stream behavior of Sm$_2$O$_3$ we found that for temperatures above 660°C, the catalyst becomes gray due to deactivation after about 1 h on stream. This is a combined effect of the lack of oxygen fed into the reactor and the depletion of lattice oxygen used for oxidation reactions. Indeed, time-on-stream experiments at 680°C show that after about 2 h on stream the conversion drops significantly because the system is limited in oxygen. The use of lattice oxygen for oxidation reactions over MgO (23) and La$_2$O$_3$ (24) has been proposed during the oxidative coupling of methane. From that work it was concluded that surface O$_2^-$ species can oxidize methyl radicals to carbon monoxide and carbon dioxide via the reaction

$$2H_3C^\bullet + 3O_2^- \rightarrow CO + CO_2 + 3H_2O. \qquad [2]$$
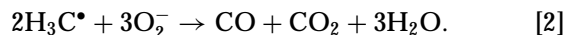
Evidently, acetonitrile at temperatures higher than about 670°C during the first 2 h is oxidized partially by lattice oxygen due to the lack of gas-phase oxygen. As will be shown below, this behavior is observed for other unpromoted oxides as well.

For the range of reaction temperatures investigated, the net amount of methane formed due to the decomposition

of acetonitrile as determined by a carbon mass balance was at trace levels. Under the present operating conditions no propionitrile was observed for any temperature. The effluent of the reactor was analyzed for the detection of bulkier nitriles (e.g., succinonitrile, adiponitrile), but no large-chain nitriles were detected as well. Acrylonitrile was observed only below 600°C and its selectivity acquired very low values. From our experiments we did not observe any C$_2$ and C$_3$ saturated or unsaturated hydrocarbons which indicates that oxidative coupling of methane reactions does not take place to any extent. Hence, for the present system it seems that acetonitrile is the reactant that is responsible for the product distribution at the temperature range involved. This is as expected because methane is a much more stable molecule than acetonitrile.

The selectivities of CO and CO$_2$ are much higher in comparison with the selectivity of acrylonitrile. This indicates that the acetonitrile is transformed over Sm$_2$O$_3$ preferably to CO$_x$ rather than any products of methylation. The sum of CO and CO$_2$ selectivities is practically unchanged for any temperature. The selectivity for carbon dioxide decreases with temperature while that of CO increases. The above observations indicate that the distribution of CO$_x$ is controlled by the water–gas shift equilibrium:

$$CO + H_2O(g) \Leftrightarrow CO_2 + H_2, \quad \Delta H_{298} = -9.784 \text{ kcal/mol}. \qquad [3]$$
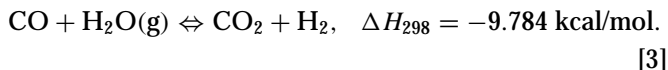
Since this reaction is exothermic, the increase in the reaction temperature will favor the reverse reaction. Another reason for the decrease in the CO$_2$ selectivity at high temperatures where the above conversion becomes 100% is that the oxygen concentration fed into the reactor is not sufficient to transform all the carbon atoms of the acetonitrile to CO$_2$. Other researchers (25, 26) came to a similar conclusion about the selectivities of CO and CO$_2$ during the oxidative coupling over Sr/La$_2$O$_3$ catalyst. Nitrogen was observed as a final product while no HCN and NH$_3$ were detected. The fact that we observe nitrogen and not hydrogen cyanide or ammonia (the latter contain one atom of nitrogen) attests that two molecules of acetonitrile react for the production of CO$_x$. Moreover, these results support our claim that the reaction proceeds via a radical mechanism but more detailed analysis was presented in another paper (27).

La$_2$O$_3$

Lunsford and co-workers (23, 28) found that La$_2$O$_3$ was the most active oxide among all the rare earth metal oxides in generating gas-phase methyl radicals (H$_3$C$^\bullet$) during OCM reactions. The radicals were collected in a solid Ar matrix and were analyzed with EPR spectroscopy. Although lanthana was the most effective oxide in generating radicals, it was very active in oxidizing C$_{2+}$ hydrocarbons (23, 28). In our study the acetonitrile conversion is about
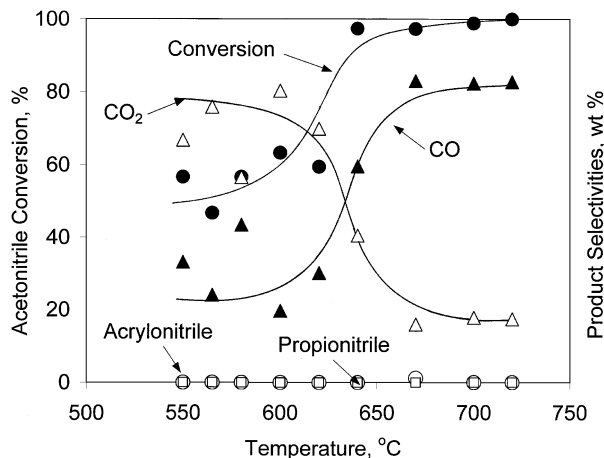
FIG. 2. Acetonitrile conversion and selectivities of CO, CO_2, acrylonitrile, and propionitrile over La_2O_3 versus reaction temperature [WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar), 1 h on stream].

50% (Fig. 2) for temperatures below 620°C; this value corresponds to the stoichiometric conversion for the oxygen fed into the reactor. However, for higher temperatures the acetonitrile conversion reaches a very high value. An explanation for the complete transformation of acetonitrile at elevated temperatures when the oxygen is the limiting reactant was presented earlier in our paper. One can observe that the temperature window for complete conversion of acetonitrile over lanthana is shifted to lower values (640°C) in comparison with samaria (680°C), thus indicating that the former oxide is more effective in oxidizing acetonitrile. This is in agreement with earlier work (23) indicating that even though La_2O_3 is very effective in generating methyl radicals it greatly favors oxidation reactions. The selectivities of CO and CO_2 with respect to the reaction temperature follow similar trends with the latter catalyst. As presented earlier, the effect of temperature on the water–gas shift equilibrium and the lack of gas-phase oxygen are responsible for these trends. The acrylonitrile generated was at very low levels for any temperature. No propionitrile and methane were produced.

Otsuka *et al.* (21) observed that alkali cations can be very effective promoters on Sm_2O_3 for the oxidative coupling of methane. It was found that the addition of Li on samaria can increase the selectivity for C_{2+} hydrocarbons. In the present study we tested the performance of Sm_2O_3 and La_2O_3 loaded with Li (Table 1) for the transformation of acetonitrile to acrylonitrile. From our catalytic experiments conducted at 680°C we found that the addition of lithium does not favor the production of acrylonitrile. However, it is worth noting that the addition of Li decreases the rate of oxidation of acetonitrile significantly in comparison with the unpromoted samaria and lanthana (compare Table 2 with Figs. 1 and 2) for the same reaction temperature. Lithium

has a positive effect by decreasing the rate of oxidation of acetonitrile, probably by blocking part of the sites that carry out the oxidation reactions. This behavior is in agreement with previous OCM studies since lanthana doped with Li (1 wt%) demonstrated higher selectivities for C_{2+} hydrocarbons than the undoped support as well (24). The chemical analyses of the catalysts (Table 1) indicate that both samaria and lanthana are not effective supports in stabilizing lithium since its concentration decreases significantly after the initial calcination step.

MgO

MgO has been tested for the methylation of acetonitrile to acrylonitrile as well. It was found (Table 3) that MgO oxidizes acetonitrile to CO and CO_2. A similar type of behavior was observed with magnesia during the oxidative coupling of methane where it demonstrated high activity for methane oxidation (29). A comparison between MgO and La_2O_3 for OCM reactions (26) has shown under identical conditions

TABLE 2

Acetonitrile Conversion and Product Selectivities over La_2O_3 and Sm_2O_3 Oxides Doped with Li for the Methylation of Acetonitrile at 680°C[a]

Catalyst	Acetonitrile conversion (%)	Selectivity (wt%)			
		CO	CO_2	Acrylo-nitrile	Propio-nitrile
Li/La_2O_3 (20 wt%)	37.1	40.1	57.5	2.4	0
Li/Sm_2O_3 (10 wt%)	46.8	49.3	50.7	0	0
Li/Sm_2O_3 (20 wt%)	56.8	54.6	45.4	0.1	0

[a] WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar), 1 h on stream.

TABLE 3

Acetonitrile Conversion and Product Selectivities over MgO Oxides Doped with Alkali Metal(s) for the Methylation of Acetonitrile at 680°C[a]

Catalyst	Alkali metal radius[b] (Å)	Acetonitrile conversion (%)	Product selectivity (wt%)			
			CO	CO_2	Acrylo-nitrile	Propio-nitrile
MgO	—	50.0	56.1	43.9	0	0
Li/MgO	0.68	39.6	0.0	68.0	30.5	1.5
Na/MgO	0.97	46.3	37.9	49.3	12.8	0
K/MgO	1.33	44.0	33.2	57.1	9.6	0
Rb/MgO	1.47	43.3	47.8	50.0	1.5	0.7
Cs/MgO	1.67	66.2	69.2	30.8	0	0

[a] WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar), 1 h on stream, alkali metal loading = 20 wt%.

[b] The ionic radii for the alkali ions are provided by the "CRC Handbook of Chemistry and Physics" (Weast *et al.*, 1988).

that the former catalyst is less effective in generating C_2 hydrocarbons. However, we observed that the performance of magnesia changes dramatically when we add lithium (Fig. 3). The conversion of acetonitrile remains at about 50% for temperatures up to 720°C. Moreover, the generation of acrylonitrile and propionitrile indicates that methane is successfully added to the methyl group of the acetonitrile. It is worth noting that the selectivity of acrylonitrile passes through a maximum for temperatures in the vicinity of 680°C and then it drops fast for temperatures higher than 720°C. This sudden drop in acrylonitrile selectivity is associated with the complete oxidation of all the organics (acetonitrile and produced nitriles, excluding CH_4) to CO and CO_2 for temperatures exceeding the above limit. The relation between acetonitrile conversion and production of acrylonitrile for temperatures below 720°C indicates that MgO doped with certain concentration of Li uses effectively acetonitrile for the production of acrylonitrile. The selectivity of CO_2 decreases with temperature. However, the selectivity of CO remains at very low levels for temperatures up to 700°C and then it increases abruptly. The oxidation of the nitriles is associated with the production of nitrogen. Hydrogen cyanide and ammonia were not detected at the exit of the reactor.

The general reactions (unbalanced) that are responsible for the nitriles produced over Li/MgO are

$$CH_3CN + CH_4 + O_2 \xrightarrow{O_2} CH_3CH_2CN + H_2$$
$$\xrightarrow{O_2} CH_3{=}CH_2CN + H_2O. \qquad [4]$$
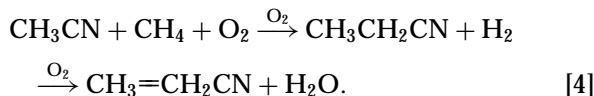
A kinetic study for the understanding of the detailed mechanism over this catalyst is presented elsewhere (27). Light hydrocarbons such as ethane or ethene as well as branched nitriles were not observed over this catalyst. This indicates that the coupling of methyl radicals with radicals formed at the α-carbon of acetonitrile effectively takes place. Moreover, the lack of C_2 hydrocarbons at the reactor effluent indicates that in the presence of acetonitrile, methane is used only for the transformation of acetonitrile to acrylonitrile. Under the same operating conditions when acetonitrile and methane were fed into the reactor, in the absence of the catalyst we did not observed any acrylonitrile and propionitrile which indicates that the catalyst is responsible for the oxidative transformation of acetonitrile to the former nitriles in the presence of methane. It should be noted that in the absence of acetonitrile, we found that Li/MgO favors the formation of C_2 hydrocarbons at considerable quantities. A white deposit was detected at the postreaction zone. FT-IR studies of this deposit after it was dissolved in tetrahydrofuran showed no peaks in the range 2500 to 2000 cm^{-1} which is characteristic for nitriles, thus indicating that no "large"-molecular-weight nitriles (e.g., succinonitrile, adiponitrile) were produced. This deposit was lithium which is volatile at
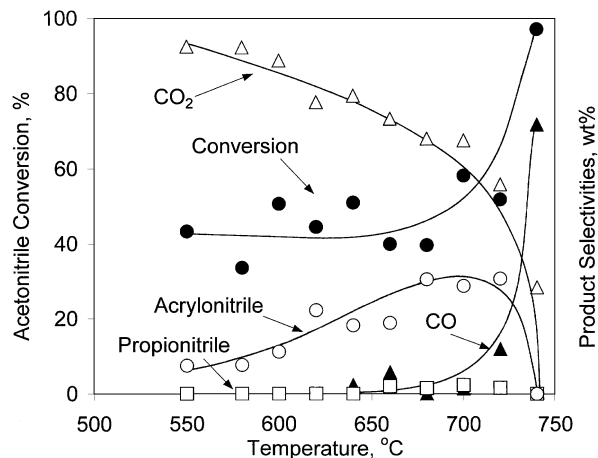

FIG. 3. Acetonitrile conversion and selectivities of CO, CO_2, acrylonitrile, and propionitrile over Li/MgO (20 wt% Li content) versus reaction temperature [WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar), 1 h on stream].

elevated temperatures. Other researchers (28, 29) claimed that over Li/MgO catalysts the presence of steam favors the sublimation of lithium.

The significant difference in the performance of Li-doped magnesia in comparison with the undoped or the other oxides presented earlier is that the former catalyst transforms the active species generated by the activation of methane and acetonitrile to acrylonitrile rather than to CO and CO_2. During the OCM reactions Lunsford and co-workers (30, 31) showed that the active sites of Li/MgO for the formation of $H_3C^\bullet$ radicals in the presence of oxygen are [Li$^+$O$^-$] surface centers which initiate the abstraction of hydrogen. Lunsford and co-workers (23) compared the rates of generation of methyl radicals over La_2O_3 and Li/MgO (7 wt%) from methane under OCM conditions and found that it is higher over lanthana for any temperature. A study of the performance of Li/MgO as a function of lithium content shows that there is an optimum level of doping that can maximimize the generation of acrylonitrile (Fig. 4). For nominal lithium contents in the vicinity of 25 wt% the selectivity of acrylonitrile passes through a maximum. This maximum of acrylonitrile is probably related to a maximum rate of generation of methyl and methylcyanide radicals occurring in this range of Li concentrations. In earlier work (31) involving Li/MgO with different Li dopings for the oxidative coupling of methane, it was found that the amount of methyl radicals passes through a maximum. Of course, the operating conditions in the study that differed from ours. Moreover, it was found (31) that the concentration of the active [Li$^+$O$^-$] surface centers that were responsible for the generation of methyl radicals (determined by EPR spectroscopy) followed exactly the same trend, thus indicating that there is probably a linear relation between radicals and these active sites. Our results demonstrate that
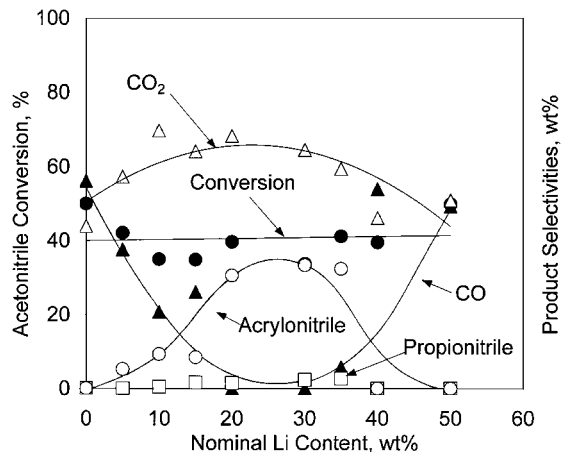
FIG. 4. Acetonitrile conversion and selectivities of CO, CO_2, acrylonitrile, and propionitrile over Li/MgO versus the nominal lithium content at $680°C$ [WHSV $= 0.92\,h^{-1}$ (based on both the organics fed into the reactor), CH_4/acetonitrile/$O_2 = 5/2/1$ (molar), 1 h on stream].

the surface sites of Li/MgO can activate both methane and the α-carbon of acetonitrile by removing a hydrogen (27). The coupling of the latter species results in propionitrile and acrylonitrile. It should be noted that Li is absolutely necessary for this reaction since MgO did not produce any of the above nitriles (Table 3, Fig. 4). Our findings with the Li/MgO catalysts for the methylation of acetonitrile to acrylonitrile and/or propionitrile and previous studies for the oxidative coupling of methane (32) suggest also that Li as promoter decreases the probability of the organic species adsorbing on the catalysts' surface and being further oxidized to CO and CO_2. However, the production of CO_x cannot be completely suppressed since gas-phase reactions of radicals with oxygen can occur as well (30).

The acetonitrile conversion remains at about 50% for any Li content (Fig. 4). The selectivity of propionitrile remains at very low levels but it passes through a broad maximum at approximately the same lithium content as the selectivity for acrylonitrile. The selectivity of CO_2 acquires a broad maximum with respect to the lithium content. The selectivity of CO passes through a minimum at lithium contents between 20 and 30 wt%. For this level of nominal Li loading we observed the highest selectivity for acrylonitrile. From this observation we propose that the generation of methylcyanide radicals which lead finally to propionitrile and acrylonitrile is associated with the existence of a maximum concentration of the active [Li^+O^-] centers. The existence of these sites probably hinders the transformation of the latter radicals to CO. The selectivity of carbon dioxide remains practically unchanged with respect to the Li content. It should be noted that the loading of lithium on magnesia decreases its surface area (Table 1). Other researchers (33) observed that the surface area of MgO can decrease up to one order of magnitude due to the loading of lithium.

The active centers for the formation of methyl radicals during OCM reactions generated over Li/MgO and detected by EPR spectroscopy (31) result from the replacement of Mg^{2+} (0.66 Å) by Li^+ (0.68 Å). This is because the substitution of a divalent ion by a monovalent ion in the lattice is associated with the generation of O^- radical ions to preserve electrical neutrality. This replacement of the alkaline earth metal by an alkali metal takes place if the radii of both cations are comparable in size. To test the effect of other alkali metals that are larger than Li we loaded Na (0.97 Å) and K (1.33 Å) on MgO. Our results (Table 3) show that the conversion over the latter catalysts is comparable to that of Li/MgO (Fig. 3) for the same loading under identical operating conditions. However, the selectivity for acrylonitrile over Na/MgO and K/MgO is three times less than in the case of Li/MgO. Experiments performed with magnesia loaded with other alkali metals having larger ionic radii indicate that the increase in the size of the alkali metal has a negative effect on the production of acrylonitrile. When Rb and Cs (20 wt%) are loaded on MgO (Table 3) we observed that the produced acrylonitrile and propionitrile became minimal. Specifically, over Cs/MgO the only products observed are CO and CO_2. These data show a monotonic decrease in the production of nitriles by the oxidative methylation of acetonitrile with the increase in the ionic radius of the alkali metal used. The above assumption for the effective substitution of Mg with the alkali metal when they are of comparable size is probably true. From the present data it seems that when "large" alkali metals are associated with magnesia, we form lattice defects that reduce the catalyst's efficiency in generating active [$M^{n+}O^-$] centers.

Bismuth-based catalysts have demonstrated good behavior for oxidative coupling of methane reactions when they are promoted with alkali metals (34) or yttria (35). In our study we tested both bismuth oxide and bismuth oxide promoted with yttria (Table 1). We found that both catalysts oxidize acetonitrile to CO and CO_2. No acrylonitrile or other nitriles were produced.

CaO was used to a less extent than MgO as support for the oxidative coupling of methane. It was found that calcium oxide promoted with alkali metals can be a good catalyst (36, 37) for the utilization of methane as well. For example if CaO ($Ca^{2+} = 0.99$ Å) is doped with sodium ($Na^+ = 0.97$ Å) the alkali metal can effectively replace the cations of the support, thus generating active [M^+O^-] centers in the lattice (38). However, the same research group could not detect [K^+O^-] species for the K/CaO catalyst. In our study several CaO-based catalysts were also tested (Table 4) for the oxidative methylation of acetonitrile to acrylonitrile under identical conditions (with other catalytic runs). CaO was found to reproducibly convert acetonitrile (about 50% conversion) to carbon monoxide and dioxide. Under the same operating conditions, CaO doped with monometallic and bimetallic combinations of alkali metals transforms

TABLE 4

Acetonitrile Conversion and Product Selectivities over CaO Oxides Doped with Alkali Metal(s) for the Methylation of Acetonitrile at 680°C[a]

Catalyst	Acetonitrile conversion (%)	Selectivity (wt%)			
		CO	CO_2	Acrylo-nitrile	Propio-nitrile
CaO	50.5	22.6	77.4	0	0
Na/CaO (5.5 wt%)[b]	100	23.3	76.7	0	0
Cs/Na/CaO (5.5/5.5 wt%)	100	32.3	67.7	0	0
Cs/K/CaO (5.5/5.5 wt%)	100	42.2	57.8	0	0

[a] WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar), 1 h on stream.
[b] The above alkali metal loadings are nominal.

acetonitrile completely to CO_x (Table 4). Nitrogen was also produced as a result of the oxidation of acetonitrile. HCN was not detected under a wide range of experimental conditions. Our investigations show that calcium oxide-based catalysts are not effective catalysts for the oxidative methylation of acetonitrile to acrylonitrile. This behavior is in contrast to what one would expect since calcium oxide-based catalysts were active for the oxidative coupling of methane reactions (39). It seems that CaO oxidizes acetonitrile very easily in comparison with methane since the former species is not as stable as methane.

The basicity of the catalysts used in this work was studied to achieve a deeper understanding of their surface characteristics responsible for the effective methylation of acetonitrile to acrylonitrile. The FT-IR patterns of the catalysts after CO_2 was adsorbed (in the range 1600 to 1200 cm^{-1}), which correspond to different types of surface carbonate species (symmetrical, monodentate, bidentate), are commonly used to characterize basic sites (40). The Li/MgO catalyst, which was the most effective catalyst for the above reactions, showed very small peaks in this range (Fig. 5) in comparison with the other catalysts used. When the same amount of sodium was added on MgO instead of lithium, the total area of these peaks slightly increased. However, the performance of Na/MgO was worse than that of Li/MgO (Table 3) under identical operating conditions, which indicates that the increase in the number of basic sites does not necessarily improve the catalyst's performance. When two alkali metals, namely, Cs and Li, were added to magnesia (Fig. 5) the height of the IR bands did not increase in comparison with Li/MgO, thus indicating that bimetallic combinations do not significantly increase the number of basic sites. An inspection of the CaO-based catalysts shows that the IR bands are much higher than in the case of the MgO-based catalysts. It is worth noting that the addition of alkali metal(s), in the present case of Na or Na and Cs, dramatically increases the number of basic sites in contrast

to undoped CaO. A comparison of the CO_2-TPD profiles of MgO- and CaO-doped catalysts with the same amount of sodium shows that the latter oxide not only possesses abundant basic sites, but those of higher strength, since the CO_2 desorption temperature was higher.

A comparison of the CaO with the CaO-doped catalysts (Table 4) shows that the increase in the number of basic sites followed by the doping of CaO (Fig. 5) increases the rate of the undesired acetonitrile oxidation. Acetonitrile possesses an electron-withdrawing group (–CN) and therefore its α-carbon is positively charged. For this reason, a catalyst with numerous and strong basic sites will significantly increase the residence time of acetonitrile on its surface and consequently favor its oxidation. Others (16) found that bimetallic combinations of alkali metals on CaO catalyze to some extent the formation of acrylonitrile. A trend different from that we observed with calcium oxide catalysts is found with samaria and lanthana, since the addition of an alkali metal decreases the number of basic sites. The curve of Li/MgO is included for quantitative comparison. Specifically, unpromoted samaria possesses numerous basic sites while Li/Sm_2O_3 does not show any basicity (Fig. 6). By correlating the catalysts' basicity characteristics with their catalytic properties at 680°C (acetonitrile conversion and product selectivities presented in Figs. 1 and 2 and Table 2), one can conclude that the existence of numerous basic sites
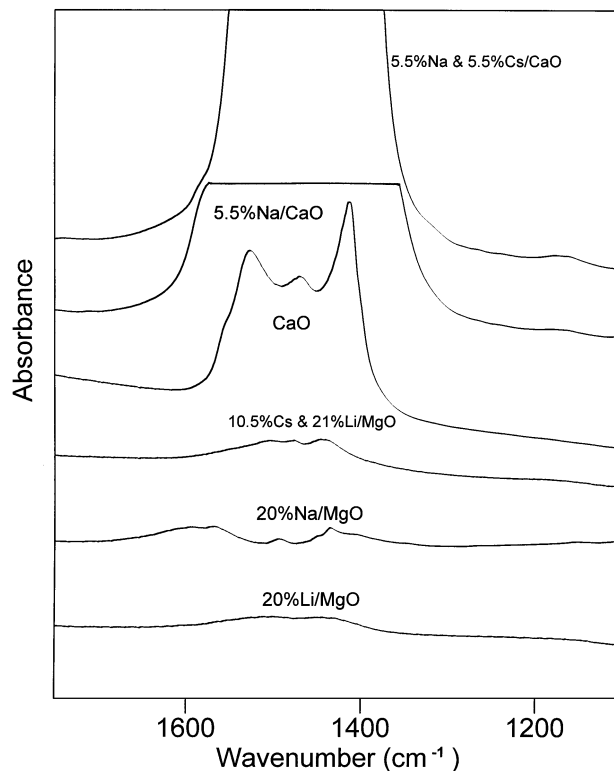

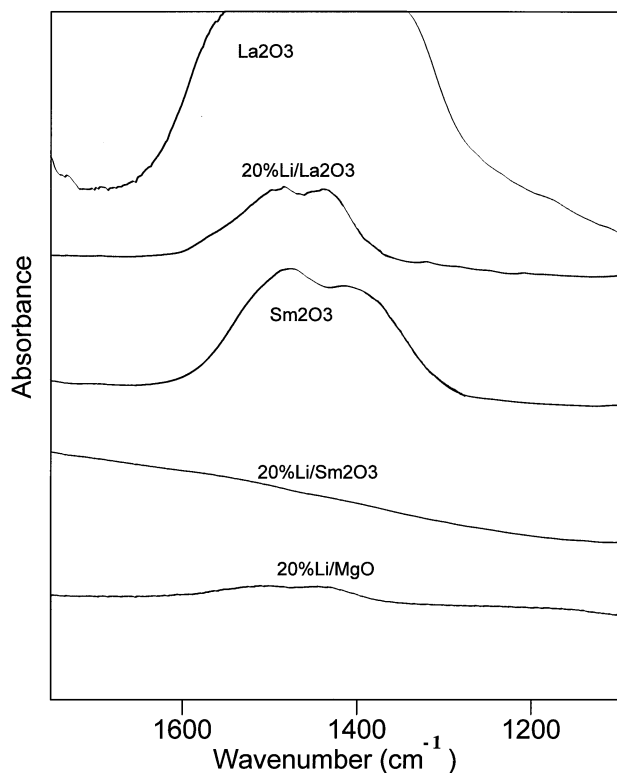**FIG. 5.** FT-IR spectra of CO_2 at 150°C over MgO- and CaO-based catalysts.

FIG. 6. FT-IR spectra of CO_2 at 150°C over Sm_2O_3- and La_2O_3-based catalysts.

has a negative effect. This is because numerous basic sites increase the residence of acetonitrile on the catalyst's surface and consequently its oxidation. Titrations with various indicators showed that all the catalysts presented in this paper, including the bimetallic combinations, were not superbasic. According to other researchers (17, 41), a superbasic material should be able to convert indicators with $pK_a \geq +26$ from their acidic form to their conjugate base.

In Table 5 we present selected CO_2 titration data for comparison purposes. These desorption experiments were performed in a TGA to ensure high accuracy during the adsorption and desorption of the probe molecule at high temperatures. The catalysts used in this table had relatively low response in the FT-IR experiments, but they exhibited

TABLE 5

CO_2 Titration Data and Desorption Distribution of Selected Catalysts as Determined from Thermogravimetric Analyses

Catalyst	CO_2 adsorbed, (mg CO_2/g cat)	Distribution of CO_2 desorbed (%)		
		150–400°C	400–700°C	700°C+
La_2O_3	2.0	7	50	43
MgO	1.0	77	16	7
Li/MgO	0.75	0	40	60

entirely different catalytic behaviors. First, one could observe that the total amount of CO_2 adsorbed (which directly corresponds to the number of basic sites) over La_2O_3 is approximately double that of MgO and Li/MgO. Moreover, the strength distribution of basic sites varies significantly for the individual catalysts. One can note that La_2O_3 and Li/MgO possess stronger basic sites (desorption of carbon dioxide at higher temperatures) than MgO. However, the performance of these catalysts as described earlier in the paper cannot be correlated with their basicity characteristics. From the results presented in this paper, it seems that the increased basicity of the catalyst plays a rather negative role for the successful methylation of acetonitrile to acrylonitrile. Although Li/MgO possessed a relatively low number of basic sites, it was the most effective catalyst for this reaction. Evidently, the $[Li^+O^-]$ surface sites are responsible for the effective transformation of acetonitrile to acrylonitrile with methane.

Bimetallic Combinations on MgO

Earlier investigations (41, 42) involving Li/MgO catalysts indicate that lanthanides (La, Ce, Nd, and Sm) were very good promoters for OCM reactions. For these dopants, the selectivity for C_{2+} hydrocarbons reached very high values and the catalysts simultaneously acquired time-stable activity. From our experiments involving La/Li/MgO and Sm/Li/MgO catalysts for the methylation of acetonitrile with 11 and 12 wt% La and Sm (Table 1), respectively, we found that doping Li/MgO with lanthanides has a very negative effect. More specifically, the only products observed at 680°C were CO and CO_2. The acetonitrile conversion under these conditions was in the vicinity of 50%. Trace amounts of acrylonitrile were generated only at the initial stages of the reaction (not shown). Evidently, a comparison of these bimetallic catalysts with the Li/MgO (20 wt% Li) shows that the addition of lanthanides causes a very negative effect on the catalyst's performance. It seems that the La and Sm cations oxidize both the acetonitrile fed into the reactor and all the nitriles produced. This result is in agreement with the behavior of Sm_2O_3 and La_2O_3 described earlier in this paper.

In our studies we incorporated praseodymium into Li/MgO catalyst as well. The acetonitrile conversion remains almost unchanged (at low level) at temperatures below 650°C while it increases monotonically at higher temperatures (Fig. 7). The selectivity of CO increases while that of CO_2 decreases with temperature. An explanation of the trends of the relative concentrations of carbon monoxide and dioxide was presented earlier in the paper. The selectivity for acrylonitrile reaches relatively low levels and becomes negligible at temperatures above 720°C. A comparison of this catalyst with Li/MgO (Fig. 3) indicates that the incorporation of praseodymium (11 wt%) has a negative effect on the catalyst's performance for the production
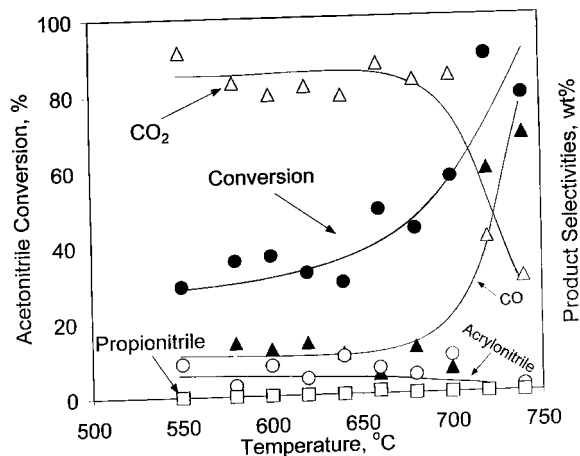
FIG. 7. Acetonitrile conversion and selectivities of CO, CO_2, acrylonitrile, and propionitrile over Pr/Li/MgO– (Pr = 11 wt%, Li = 22 wt%) versus reaction temperature [WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar), 1 h on stream].

TABLE 6

Acetonitrile Conversion and Product Selectivities over MgO Loaded with Bimetallic Combinations of Alkali Metals for the Methylation of Acetonitrile at 680°C[a]

Catalyst	Acetonitrile conversion (%)	Selectivity (wt%)			
		CO	CO_2	Acrylo-nitrile	Propio-nitrile
Na/Li/MgO (0.5/20 wt%)	29.7	2.2	73.3	22.6	1.9
K/Li/MgO (0.5/20 wt%)	27.0	7.4	65.6	23.9	3.0
Rb/Li/MgO (0.5/22 wt%)	29.8	7.9	67.9	21.7	2.4
Cs/Li/MgO (0.5/22 wt%)	39.3	10.3	65.2	21.9	2.6
Pr/Li/MgO (0.5/22 wt%)	32.5	4.6	59.2	34.5	1.7

[a] The concentration of Li was about 20%. WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar), 1 h on stream.

of acrylonitrile. This is not as expected since earlier studies (43) indicated that a combination of praseodymium with alkali metals and/or alkaline earth metals results in a very effective catalyst for OCM reactions. A similar type of performance was observed when cesium was loaded on Li/MgO (Cs content = 10.5 wt% Li content = 21 wt% at temperatures varying in the same range (Fig. 8). The selectivity of acrylonitrile remains at relatively low levels which are comparable to those observed with the Pr/Li/MgO catalyst. However, the acetonitrile conversion over the Cs/Li/MgO catalysts is lower than in the previous case in the same temperature range. One can conclude that by doping Li/MgO with relatively large concentrations of Pr or Cs, the cata-
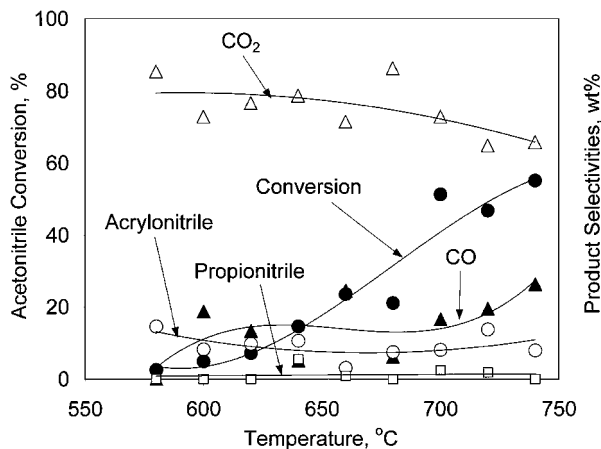
lysts' performance decreases in comparison with Li/MgO loaded with the same amount of lithium. It seems that the Cs or Pr probably results in partial covering of the active surface of the catalyst.

MgO-based bimetallic catalysts with lithium content in the range of about 20 wt% and small amounts of the second metal (0.5 wt%) were tested as well (Table 6). The concentration of Li remained in the vicinity of 20 wt% because we found (Fig. 3) that this level of Li loading demonstrates optimum behavior. A comparison of the data presented in Table 6 with the results for Li/MgO (Li content 20 wt%) indicates that the addition of even small amounts of an alkali metal as a dopant (0.5 wt%) does not improve the effectiveness of the catalyst for the production of acrylonitrile. When the catalyst is doped with Na, K, and Rb both the acetonitrile conversion and the selectivity of acrylonitrile are lower than those of Li/MgO catalyst. When Cs and Pr are added to the Li/MgO, the yield of acrylonitrile approaches that of Li/MgO. The effectiveness of the catalyst doped with Pr approaches that of Li/MgO since both the acetonitrile conversion and selectivity to acrylonitrile are slightly lower than those of the Pr-free catalyst. Our observations from the above bimetallic systems indicate that the addition of a second metal has an adverse effect. For all the above experiments, no HCN was detected. It should be noted that MgO was the most effective support in stabilizing the promoters used (Table 1).

Time-on-Stream Behavior of Li/MgO

It follows from our study that the best catalyst for the oxidative methylation of acetonitrile to acrylonitrile is Li/MgO with a nominal concentration of lithium in the vicinity of 25 wt%. For this reason the time-on-stream (TOS) behavior of the Li/MgO (20 wt%) was investigated. The conversion of acetonitrile and the selectivities of CO, CO_2, acrylonitrile, and propionitrile are presented in Fig. 9
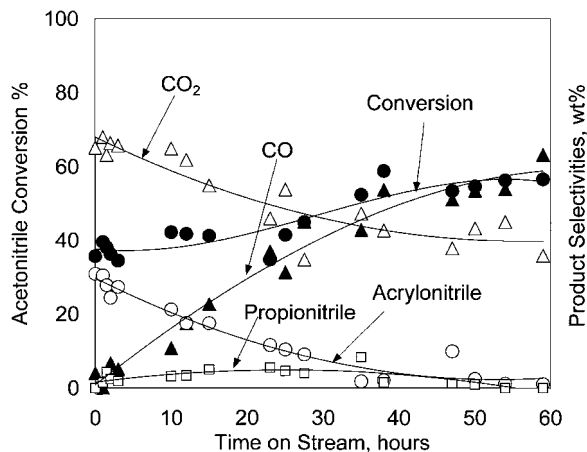

FIG. 8. Acetonitrile conversion and selectivities of CO, CO_2, acrylonitrile, and propionitrile over Cs/Li/MgO (Cs = 10.5 wt%, Li = 21 wt%) versus reaction temperature [WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar), 1 h on stream].

FIG. 9. Acetonitrile conversion and selectivities of CO, CO_2, acrylonitrile, and propionitrile over Li/MgO (Li = 20 wt%) versus time on stream at 680°C [WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar)].

as a function of time on stream for a period of 60 h. The conversion of acetonitrile increases monotonically with time on stream and acquires a value of about 60% at the end of the run. The selectivity of CO is low for time on stream less than about 10 h. However, for a longer time on stream it increases monotonically. The selectivity of acrylonitrile acquires relatively high values in the initial 15 h but it decreases monotonically afterward. At the end of the run the selectivity of acrylonitrile is very low. We believe that this behavior can be attributed to the large decrease in the Li content after the initial stages of the reaction. As one can observe in Table 7, the nominal lithium content of the catalysts after the initial calcination step (14 h at 700°C) decreases significantly; namely, from 20 wt% it drops to 13.5 wt%. Other researchers (44, 45) found that at elevated temperatures and in the presence of steam, Li

TABLE 7

Lithium Content and BET Surface Area of the Li/MgO Catalyst as a Function of Time on Stream during the Oxidative Methylation of Acetonitrile with Methane at $T = 680°C^a$

Time on stream (h)	Li concentration[b] (wt%)	BET surface area (m²/g)
Nominal composition	20.0	5.7
after the calcination	13.5	2.1
1	7.1	0.6
28	2.2	0.3
60	0.4	Below detection limits

[a] Nominal concentration of Li = 20 wt%. WHSV = 0.92 h^{-1} (based on both the organics fed into the reactor), CH_4/acetonitrile/O_2 = 5/2/1 (molar).
[b] The Li concentration reported in this table is determined by excluding the chloride atoms of the sample.

easily sublimes. Indeed, we detected lithium deposits in the postreaction zone. After 28 h on stream the concentration of lithium on the catalyst drops to about 2 wt%, while after 60 h on stream lithium practically disappears from the catalyst (0.4 wt%). In addition, to the significant decrease in lithium content as a function of time on stream, the BET surface area significantly decreased.

The gradual change in the state of the catalyst is responsible for the CO and CO_2 trends observed. The selectivity of CO_2 acquires relatively high values at the beginning of the catalytic run, namely, about 65%, and decreases monotonically with time on stream. The opposite trend was observed for CO. At the initial stages of the reaction the CO generated is low, then it increases monotonically with time on stream and finally approaches a plateau value at about 60 wt%. It is worth noting that experiments performed with pure MgO under conditions identical to those of the TOS experiments indicate that acetonitrile is transformed only to CO, CO_2, and N_2. The selectivities of CO and CO_2 were 56.1 and 43.9%, respectively (Table 3). Those values were very comparable to the corresponding values of carbon monoxide and dioxide at the end of the "time-on-stream" experiment over the Li/MgO catalyst (Fig. 9). This indicates that the continuous decrease in Li content of the catalysts is responsible for the gradual change in product distribution. The earlier observations from the doping of samaria and lanthana with lithium (Table 2, Figs. 1 and 2) indicate that lithium decreases the rate of the nitrile oxidation reactions. The present behavior is sound evidence that Li is absolutely necessary for the selective methylation of acetonitrile to acrylonitrile and the suppression of the undesired oxidation of acetonitrile or the produced nitriles.

CONCLUSIONS

Our study shows that Li/MgO catalysts are effective catalysts for the oxidative methylation of acetonitrile to acrylonitrile with methane. An optimum concentration of lithium that maximizes the generation of acrylonitrile exists and it is probably associated with a maximum concentration of [Li$^+$O$^-$] surface centers. The additional role of Li on magnesia is to hinder oxidation reactions of acetonitrile. It is worth noting that it is the combination of lithium with magnesia that results in effective catalysts. The addition of a second metal to Li/MgO has a negative effect on catalyst performance. Undoped MgO or lithium on other oxides (other than MgO) does not exhibit any significant selectivities for acrylonitrile. Numerous catalysts that are very effective in generating methyl radicals and thus favoring the oxidative coupling of methane to C_{2+} hydrocarbons were tested. It was found that they are not efficient for the above reaction. It was concluded that the basicity of the supports or the catalysts was not an essential factor for the oxidative methylation of acetonitrile with methane.

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