

# Oxidative methylation of $\alpha$ -, $\beta$ - and $\gamma$ -picolines with methane vinylpyridines and ethylpyridines over mono- and bialkali promoted magnesia catalysts

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Received 26 April 1994; accepted 15 July 1994

The oxidative methylation of  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines with methane to the corresponding vinyl- and ethylpyridines was carried out at 750°C and under normal atmospheric pressure, over sodium, cesium or sodium–cesium promoted magnesia catalysts. Among the three picolines, the  $\gamma$ -picoline was the most reactive, followed by  $\alpha$ - and  $\beta$ -picolines. The (5 mol% Na–5 mol% Cs)/MgO catalyst provided higher yields than the individual promoters, at the same total alkali content of 10 mol%.

**Keywords:** picolines; methane; methylation; alkali promoted magnesia

## 1. Introduction

The high molecular stability of methane makes difficult its conversion to other useful chemical feedstocks. The development of catalytic processes for the conversion of methane to more reactive chemicals, such as methanol, ethylene, and other higher hydrocarbons is of importance. Among them, the oxidative coupling of methane to ethane and ethene ( $C_2$  compounds) has received a great deal of attention; many metal-oxide-based catalysts promoted with various compounds have been investigated [1–3] in this direction. Another use of methane is its coupling with other chemicals such as nitriles, alkenes, and alkyl-substituted aromatic compounds to produce more valuable products. However, such attempts have been much fewer in number. Khcheyan et al. [4] reported that mixtures of oxides of bismuth, molybdenum and zinc promoted with either alkali or alkaline earth compounds were active and selective in the oxidative methylation of toluene with methane to styrene and ethylbenzene ( $C_8$  hydrocarbons). Using the same catalysts, they also reported the formation of acrylonitrile during the oxidative methylation

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of acetonitrile with methane. Suzuki et al. [5,6] have noted that basic oxide catalysts, including rare earth oxides, promoted with alkali or alkaline earth halides, were active and selective in the formation of  $C_8$  hydrocarbons from methane and toluene. The silica supported potassium bromide [7], the lithium-promoted  $Y_2O_3$ -CaO [8], the PbO-MgO [9], and the PbO/Li/MgO catalysts [10] were also found to provide good activities and selectivities for the formation of  $C_8$  from toluene and methane. Recently, we have reported that basic oxides (MgO or CaO), promoted with monoalkali (Li, Na, K, Cs, Rb) and particularly with bialkali were very active and selective in the oxidative methylation of toluene [11] and acetonitrile [12] with methane to styrene/ethylbenzene and acrylonitrile/propionitrile, respectively. The bialkali promoted catalysts have been the most efficient, because of the synergism they exhibited. Among various bialkali promoters, the  $Na^+$ - $Cs^+$  combination provided the highest activity and selectivity in both reactions. The (5 mol% Na + 5 mol% Cs)/MgO catalyst possessed a much higher activity and selectivity than either 10 mol% Na/MgO or 10 mol% Cs/MgO catalysts. Since the picolines contain, as toluene and acetonitrile do, an electron-withdrawing functional group, it is likely that similar catalysts could be useful in the oxidative methylation of the picolines.

In this study we report the results obtained regarding the oxidative methylation of  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines to their corresponding vinyl- and ethylpyridine compounds.

## 2. Experimental

### 2.1. CATALYST PREPARATION

MgO (99+%), NaOH (99.99%) and CsOH (99+%) were obtained from Aldrich. The MgO was further washed with double-distilled water, dried at 120°C for 18 h, and calcined at 750°C for 15 h. Onto the calcined MgO, mono (NaOH or CsOH, 10 mol%) or bialkali (5 mol% NaOH + 5 mol% CsOH) promoters were deposited by wet impregnation, using an aqueous slurry of MgO, under vigorous stirring. The resulting slurry was heated on a hot plate until a thick paste was generated, which was further oven dried at 120°C for 16 h and finally calcined in air at 750°C for 15 h. The calcined powdered catalysts were pressed, crushed and sieved to 80–100 mesh for the catalytic studies.

### 2.2. CATALYST TESTING

The catalytic experiments were carried out at atmospheric pressure, in a high-purity alumina tube (6 mm i.d., 30 cm long) mounted horizontally and heated by a programmable single-zone electric furnace containing a built-in thermocouple. The catalyst (0.4 g) was located at the middle of the reactor between two quartz

wool plugs. All gases used were high purity grade (Cryogenic Supply, >99.9% purity) and were employed as received. The picoline reactants were research grade (Aldrich) and were used without further purification. The inlet and outlet lines were of stainless steel protected with heating tapes to avoid condensation.

The reaction conditions employed were: pressure, atmospheric; reaction temperature, 750°C; amount of catalyst, 0.4 g; flow rate of the gas mixture, 50 ml/min; partial pressure ratios,  $P(\text{CH}_4) : P(\text{O}_2) : P(\text{C}_6\text{H}_7\text{N}) : P(\text{He}) = 15.1 : 3 : 1 : 12.1$ , and space velocity (GHSV),  $7500 \text{ h}^{-1}$ .

The picoline was introduced into a preheated zone (250°C) with a liquid feed pump (KD Scientific), where it was mixed with the gases involved in the reaction. The flow rates of the latter were controlled with variable constant differential flow controllers (Porter VCD 1000). The feed gases and gaseous products were analyzed on-line, using a 10-port sampling valve and analyzed with a gas chromatograph (Perkin-Elmer, Sigma 2000) fitted with thermal conductivity and flame ionization detectors. The liquid products condensed in a heptanol–liquid nitrogen (−40°C) trap were analyzed using two gas chromatographs, a Perkin Elmer Sigma 2000, fitted with a FID detector and an Apiezon L Column (3.2 mm × 2.64 m), and a GC-MS (HP 5890) fitted with a mass-selective detector (5971A) and three columns: a molecular sieve 5A (3.2 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). The conversions of the picolines are expressed as the fractions of picolines converted. 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 percent yield of vinylpyridine is the product of the conversion of picoline and the selectivity.

### 3. Results and discussion

In the oxidative methylation of picoline with methane, the main reaction products observed were pyridine (Py), ethylpyridine (EP), vinylpyridine (VP), carbon oxides (CO and CO<sub>2</sub>) and water, with small amounts of lutidines, ethylmethylpyridine, pyridine carboxaldehyde, C<sub>2</sub> hydrocarbons and traces of unidentified hydrocarbons. The results of the methylation of the  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines with methane over MgO and alkali-promoted MgO catalysts are summarized in tables 1, 2 and 3, respectively. One can note from these tables that small yields (0.5–0.6%) were obtained with the reactor free of catalyst but containing quartz wool plugs. While the yields are insignificant when compared to those involving the catalysts, some methylation of the picoline has taken place thermally. The MgO catalyst provided a C<sub>7</sub> (EP + VP) product selectivity ranging from 13.0 to 15.0%. The yield of C<sub>7</sub> was, however, low (1.8–2.1%). While these values are higher than those in the non-catalytic reactions, they are much lower than those over the mono- or bialkali promoted catalysts. A comparison of the oxygen and methane conversions over MgO

Table 1  
Oxidative methylation of  $\alpha$ -picoline with methane over alkali promoted MgO<sup>a</sup>

Catalyst (alkali in mol%)	Conversion (%)			Selectivity (%)			C <sub>7</sub> yield (%) ( $\alpha$ -EP + $\alpha$ -VP)
	C <sub>6</sub> H <sub>7</sub> N	O <sub>2</sub>	CH <sub>4</sub>	$\alpha$ -EP	$\alpha$ -VP	total C <sub>7</sub> <sup>b</sup> ( $\alpha$ -EP + $\alpha$ -VP)	
quartz wool	5.8	55	1.8	4.2	2.7	6.9	0.4
MgO	14.2	96	2.4	8.0	6.4	14.4	2.0
10% Na <sup>+</sup> /MgO	22.2	95	8.2	21.2	25.0	46.2	10.2
10% Cs <sup>+</sup> /MgO	24.4	98	9.9	20.4	28.8	49.2	12.0
(5% Na <sup>+</sup> + 5% Cs <sup>+</sup> )/MgO	31.4	98	12.1	20.3	30.0	50.3	15.8

<sup>a</sup> Reaction conditions:  $T = 750^\circ\text{C}$ ,  $p = 1$  atm, total flow rate 50 ml/min (NTP),  $P(\text{CH}_4) : P(\text{O}_2) : P(\text{C}_6\text{H}_7\text{N}) : P(\text{He}) = 15.1 : 3 : 1 : 12.1$ , and the space velocity (GHSV) =  $7500 \text{ h}^{-1}$ .

<sup>b</sup> Total selectivity for  $\alpha$ -ethylpyridine +  $\alpha$ -vinylpyridine.

<sup>c</sup> Pyridine.

Table 2  
Oxidative methylation of  $\beta$ -picoline with methane over alkali promoted MgO<sup>a</sup>

Catalyst (alkali in mol%)	Conversion (%)			Selectivity (%)				C <sub>7</sub> yield (%) ( $\beta$ -EP + $\beta$ -VP)
	C <sub>6</sub> H <sub>7</sub> N	O <sub>2</sub>	CH <sub>4</sub>	$\beta$ -EP	$\beta$ -VP	total C <sub>7</sub>	CO <sub>x</sub>	
quartz wool	5.1	53	1.8	3.8	2.1	5.9	66.2	0.3
MgO	13.8	94	2.0	7.8	5.2	13.0	46.6	1.8
10% Na <sup>+</sup> /MgO	18.4	95	8.1	19.1	24.9	44.0	23.9	8.1
10% Cs <sup>+</sup> /MgO	20.8	97	9.8	18.2	24.4	42.6	24.2	8.9
(5% Na <sup>+</sup> + 5% Cs <sup>+</sup> )/MgO	27.6	98	11.6	21.3	29.0	50.3	21.3	13.9

<sup>a</sup> Reaction conditions and other details are as in table 1.

Table 3  
Oxidative methylation of  $\gamma$ -picoline with methane over alkali promoted MgO<sup>a</sup>

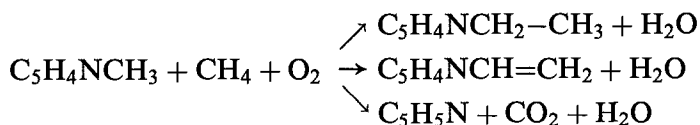
Catalyst (alkali in mol%)	Conversion (%)		Selectivity (%)		C <sub>7</sub> yield (%)		
	C <sub>6</sub> H <sub>7</sub> N	O <sub>2</sub>	CH <sub>4</sub>	$\gamma$ -EP	$\gamma$ -VP	total C <sub>7</sub>	( $\gamma$ -EP + $\gamma$ -VP)
quartz wool	6.1	54	1.7	4.1	3.8	7.9	0.5
MgO	14.2	95	2.3	8.4	6.6	15.0	2.1
10% Na <sup>+</sup> /MgO	25.9	96	8.4	20.1	25.4	45.0	11.8
10% Cs <sup>+</sup> /MgO	29.4	98	10.8	19.0	26.1	45.1	13.2
(5% Na <sup>+</sup> + 5% Cs <sup>+</sup> )/MgO	36.1	98	12.1	21.6	29.0	50.6	18.3

<sup>a</sup> Reaction conditions and other details are as in table 1.

and over alkali promoted MgO catalysts reveals that MgO is responsible for oxygen activation, while the alkali appear to promote methane activation. Due to the homolytic coupling of methane to C<sub>2</sub> products, small excesses of methane and oxygen conversions were obtained compared to those expected for the oxidative methylation of picolines. Upon promoting MgO with Na<sup>+</sup>- and Cs<sup>+</sup>-hydroxide (5 mol% + 5 mol%), significant increases in the C<sub>7</sub> selectivities and yields were observed, compared to those obtained with MgO promoted with either 10 mol% Na or 10 mol% Cs. It is clear that the synergism found in our previous papers concerning the methane coupling [13] and methylation [11,12] of toluene and acetonitrile is also present in the methylation of picolines. The highest C<sub>7</sub> yield has been 18.3% for the  $\gamma$ -picoline, 15.8% for  $\alpha$ -picoline and 13.9% for  $\beta$ -picoline. The order of the picoline reactivities towards methylation is as follows:  $\gamma$ -picoline >  $\alpha$ -picoline >  $\beta$ -picoline. The reactivity of the picolines is probably due to the competition between steric and electronic factors. The electronic factor may alone explain the observed differences in the reactivities of the picolines. The higher conversions of the  $\gamma$ - and  $\alpha$ -picolines may be due to resonance stabilization of intermediates (the pyridyl-methylene radicals). The radical intermediate generated from  $\beta$ -picoline has no such resonance stabilization.

The higher activity and selectivity of the bialkali promoted systems was related to the higher enrichment of the surface with alkali atoms, when two species are employed rather than one, as evidenced by XPS measurements [11,13]. This higher enrichment of the surface with alkali probably makes the catalyst surface more basic. They may exhibit superbasicity and from previous titration of the surface with a dilute solution of benzoic acid in the presence of various indicators, we concluded that the catalyst (5 mol% Na + 5 mol% Cs)/MgO was superbasic. The titration, particularly for high basicity, is difficult to perform, since small traces of moisture in the titrating solvents or in the indicators may result in inaccurate measurements. In fact, in more recent titration measurements, we could not detect any change in the color of the indicator with a pK<sub>a</sub> of 26.5, which indicates superbasicity [14], but only with the one with the pK<sub>a</sub> = 18.4.

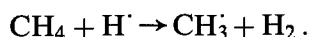
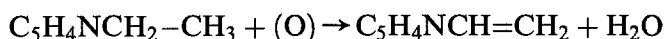
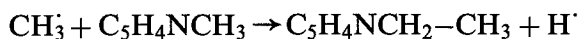
The oxidative methylation of picolines with methane yields, in addition to ethylpyridines and vinylpyridines, also pyridine and carbon oxides. The reactions are



In order to gain some information about the mechanism of picoline methylation with methane, a few additional experiments were conducted under identical reaction conditions, but in the absence of methane in the feed. Even in the absence of methane in the feed, small amounts of ethyl- and vinylpyridines were observed. This indicates that there are at least two parallel mechanisms that operate over the catalyst surface: (i) the oxidative methylation of picoline to ethylpyridine, followed by its oxidative dehydrogenation to vinylpyridine; and, to a smaller extent,

(ii) the oxidative disproportionation of picoline to pyridine and ethylpyridine, followed by the oxidative dehydrogenation of the latter molecules to vinylpyridine.

The reactive intermediates involved in the oxidative methylation of picolines with methane are the radicals  $\text{CH}_3^\cdot$ ,  $\text{C}_5\text{H}_4\text{NCH}_2^\cdot$  and  $\text{HO}_2^\cdot$  [4]. The methyl and picoline radicals are formed via the abstraction of hydrogen from methane and picoline, respectively. The coupling of these two radicals is responsible for the generation of ethylpyridine,  $\text{CH}_3^\cdot + \text{C}_5\text{H}_4\text{NCH}_2^\cdot \rightarrow \text{C}_5\text{H}_4\text{NCH}_2\text{—CH}_3$ , which is followed by the oxidative dehydrogenation to vinylpyridine ( $\text{C}_5\text{H}_4\text{NCH=CH}_2$ ). Another possibility is the generation of ethylpyridines via the direct reaction of the methyl radical with the picoline, followed by the oxidative dehydrogenation to vinylpyridines,



#### 4. Conclusions

The  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines undergo oxidative methylation with methane over the alkali promoted magnesia catalysts, producing the corresponding vinyl- and ethylpyridines. The bi-alkali (5 mol% Na–5 mol% Cs)/MgO catalyst provides higher yields than the corresponding monoalkali promoted catalyst at the same total alkali loading of 10 mol%.

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