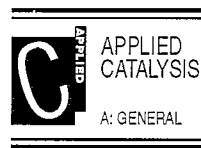




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Applied Catalysis A: General 121 (1995) 159–167



Oxidative methylation of organic compounds with methane over alkali promoted MgO catalysts

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Received 19 July 1994; revised 12 September 1994; accepted 12 September 1994

Abstract

The oxidative methylation of acetone, acetophenone and diphenylmethane with methane has been investigated over sodium, cesium and sodium–cesium promoted magnesia catalysts at 750°C and under normal atmospheric pressure. All these compounds do react with methane and produce their corresponding methane coupling products. The bi-alkali (5 mol-% Na–5 mol-% Cs) promoted MgO catalyst provided higher product yields than the individual mono-alkali promoted MgO catalysts at the same alkali content of 10 mol-%.

Keywords: Acetone; Acetophenone; Alkali promoted magnesia; Diphenylmethane; Magnesia; Methane; Oxidative methylation

1. Introduction

The direct conversion of methane into chemical feedstock or transportable liquid fuel is an attractive process. The tremendous interest in methane conversion to higher hydrocarbons is due to the underutilization of this abundant natural resource and the high costs associated with its transportation, particularly from remote places, where it is a surplus. Remarkable progress has been achieved in the last decade since the early reports of Keller and Bhasin [1] for the direct oxidative coupling of methane towards more valuable hydrocarbon products (C_{2+}) [1–6]. In addition to the homo-coupling of methane, the oxidative methylation of alkenes, nitriles, and alkyl-substituted aromatic compounds with methane to produce more valuable products is another equally important method for the efficient utilization of methane. However, such attempts are very few in the literature.

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Kcheyan et al. [7] were the first to report that mixtures of oxides of bismuth, molybdenum and zinc together with alkali and alkaline earth metals are active and selective catalysts for the oxidative methylation of toluene with methane to styrene and ethylbenzene (C_8 hydrocarbons). Using the same catalyst combinations, they also reported the formation of acrylonitrile during the oxidative methylation of acetonitrile with methane. On the basis of catalysts used for the oxidative dimerization of methane to C_2 hydrocarbons, some research groups [8–13] have used the same methane coupling catalysts for the oxidative methylation of toluene with methane to styrene/ethylbenzene. Recently, we have reported that alkaline earth oxides, such as MgO and CaO, promoted with mono-alkali (Li, Na, K, Cs, and Rb) and particularly with bi-alkali (Li–Na, Li–K, Na–K, etc., i.e., combination of any two), which are very active and selective for the oxidative coupling of methane [14], are also very active and selective for the oxidative methylation of toluene with methane to styrene/ethylbenzene [15], acetonitrile to acrylonitrile/propionitrile [16], and picolines to vinylpyridines/ethylpyridines [17], respectively. Those studies revealed that oxidative methylation with methane is possible with substrates having a methyl group attached to an electron withdrawing group. Among the various bi-alkali promoters, the Na^+--Cs^+ combination provided the highest activity and selectivity in all the reactions. The (5 mol-% $Na^+ + 5$ mol-% Cs^+)/MgO catalyst exhibited higher activity and selectivity than either 10 mol-% Na^+ / MgO or 10 mol-% Cs^+ / MgO , because of the synergism it possesses.

The present paper contains the results of the investigations on the oxidative methylation of acetone (CH_3COCH_3), acetophenone ($C_6H_5COCH_3$), and diphenylmethane ($C_6H_5CH_2C_6H_5$) with methane over the mono-alkali (10 mol-% Na^+ and 10 mol-% Cs^+) and bi-alkali (5 mol-% $Na^+ + 5$ mol-% Cs^+) promoted MgO catalysts.

2. Experimental

2.1. Catalyst preparation

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

2.2. Catalytic runs

The details regarding the reactor setup, catalyst screening, product analysis and catalyst characterization have been described previously [15]. The catalytic runs were carried out at a temperature of 750°C, under atmospheric pressure, in a high-purity alumina tube (6 mm I.D., 30 cm long) mounted vertically and heated by a programmable single-zone electric furnace containing a built-in thermocouple. The catalyst sample (0.5 g) was located at the middle of the reactor between two quartz wool plugs. All gases used were research grade (Cryogenic Supply, >99.9% purity) and were employed as received. The flow-rate of each gas was controlled by a variable constant differential flow controller (Porter VCD 1000) connected to a filter (Nupro, 7 μm) and a check valve. The total flow-rate of the gas mixture measured at the outlet of the reactor was 50 ml/min. (NTP) and the mixture composition was adjusted in such a way that conversion of oxygen was generally higher than 80%. The reactants used in this study were high purity grade (Aldrich) and were used without further purification. The reactants were introduced into a preheating zone (250–300°C) with a liquid feed pump (Cole-Parmer, 74900 series) where it was mixed with the gases involved in the reaction. All the inlet and outlet lines of the reactor were of stainless steel protected with heating tapes to avoid condensation. The gaseous products, after being separated from condensed products by passing through either a heptanol–liquid nitrogen or salt–ice bath, were sampled on-line using an automatic 10 port sampling valve (Valco) and analyzed by a gas chromatograph (Perkin-Elmer Sigma 2000) fitted with thermal conductivity and flame ionization detectors and attached to a Perkin-Elmer 3600 data station. The condensed products were analyzed off-line by a GC/MS (Hewlett-Packard 5890 Series II) equipped with a mass-selective detector (MSD 5971A). A PC unit was attached to the GC/MS for data manipulation. The GC/MS was fitted with a molecular sieve packed column (5A), a high-performance capillary column (HP-1 crosslinked methyl silicone, 0.2 mm I.D., 12 m length, and film thickness of 0.33 μm), and a fused-silica poraPLOT wide bore capillary column (0.53 mm I.D., 28 m long, and film thickness of 20 μm). The conversion is expressed as the fraction of moles of a reactant reacted. 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 is the product of the conversion of acetone, acetophenone and diphenylmethane, respectively, and the selectivity.

3. Results and discussion

The N_2 BET surface area of the pure MgO after calcination at 750°C was 14.5 $\text{m}^2 \text{g}^{-1}$. Upon impregnation with Na^+ , Cs^+ and $\text{Na}^+ - \text{Cs}^+$ promoters, the surface areas decreased to 8.2, 8.0 and 7.0 $\text{m}^2 \text{g}^{-1}$, respectively. The differences between the surface areas of monoalkali promoted catalysts and the bialkali promoted cat-

Table 1

Oxidative methylation of acetone (C_3H_6O) with methane over alkali promoted MgO. Reaction conditions: temperature $750^\circ C$, pressure atmospheric, amount of catalyst 0.5 g, total flow-rate 50 ml/min (NTP), $P(CH_4):P(O_2):P(C_3H_6O):P(He) = 9.5:1.5:1:7.6$. The results were obtained after 3 h of reaction

Catalyst (alkali in mol-%)	Conversion (%)		Selectivity (%)				C ₄ Yield (%) (MEK + MVK)		
	C ₃ H ₆ O	O ₂	CH ₄	C ₄ H ₈ O (MEK) ^a	C ₄ H ₆ O (MVK) ^b	Total C ₄ (MEK + MVK)	SP ^c	CO _x (x = 1, 2)	
10% Na ⁺ /MgO	32.6	98	6.9	11.9	13.9	25.8	28.2	40.4	8.4
10% Cs ⁺ /MgO	32.0	97	7.1	11.7	13.6	25.3	27.4	40.8	8.1
(5% Na ⁺ + 5% Cs ⁺)/MgO	36.0	98	8.1	13.1	15.2	28.3	26.4	38.4	10.2
MgO	12.2	93	2.4	7.9	6.8	14.7	26.2	52.6	1.8
Quartz wool	4.2	55	1.2	1.6	0.8	2.4	21.8	70.2	0.1

^a MEK = methyl ethyl ketone.

^b MVK = methyl vinyl ketone.

^c SP = side products include acetaldehyde, C₂, C₃ and C₄ hydrocarbons.

alysts can be considered insignificant, in view of the approximations involved in the BET method, particularly for low surface areas.

Results of the oxidative methylation of acetone (CH_3COCH_3) with methane over alkali-promoted MgO catalysts are presented in Table 1. The main reaction products observed were methyl ethyl ketone (or 2-butanone, $C_2H_5COCH_3$), methyl vinyl ketone (or 3-buten-2-one, $H_2C=CHCOCH_3$), carbon oxides (CO and CO₂) and water, with some amounts of acetaldehyde (CH_3CHO), C₂, C₃ and C₄ hydrocarbons and traces of unidentified products. As can be seen from Table 1, compared to the 10% Na⁺/MgO or 10% Cs⁺/MgO catalysts, a somewhat higher acetone conversion and C₄ (MEK + MVK) product yield were observed over the (5% Na⁺ + 5% Cs⁺)/MgO catalyst. The MgO pure catalyst provided a C₄ product selectivity of 14.7 and the yield was 1.8. 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. Very small amounts of C₄ products were obtained with the reactor free of catalyst but containing the quartz wool plugs. This indicates that some methylation of acetone takes place thermally. However, the yields obtained are insignificant when compared to those involving the catalysts. In Fig. 1, the change of C₄ product yield over the mono- and bialkali promoted MgO catalysts is presented as a function of reaction time. There is no substantial change in the product yield during the 600 min time-on-stream. The stability with time-on-stream for the bialkali systems is even higher than that for the mono-alkali systems.

The results of the oxidative methylation of acetophenone ($C_6H_5COCH_3$) over the mono- and bialkali-promoted magnesia catalysts are shown in Table 2. In the oxidative methylation of acetophenone with methane, the main reaction products were propiophenone ($C_6H_5COC_2H_5$), 1-indanone (cyclization product of $C_6H_5COCH=CH_2$), carbon oxides (CO and CO₂) and water, with small amounts of benzaldehyde (C_6H_5CHO), acetaldehyde, benzene, toluene, benzophenone, C₂,

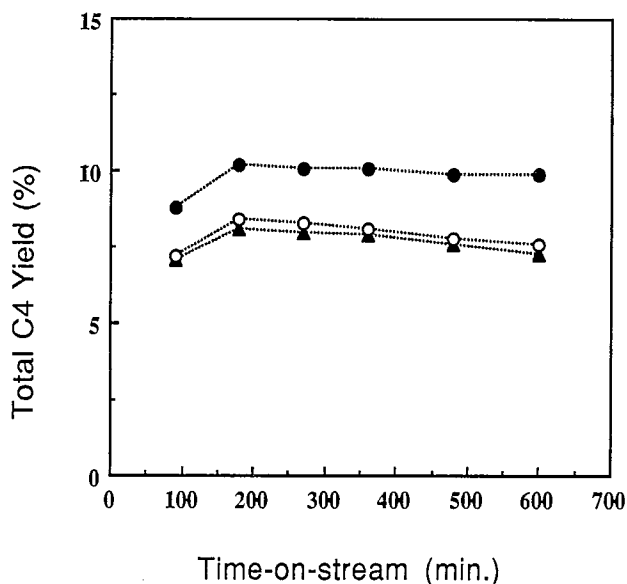


Fig. 1. The change in the C₄ product yield with time-on-stream in the oxidative methylation of acetone with methane over alkali promoted MgO catalysts. Reaction conditions as in Table 1. (○) 10 mol-% Na⁺/MgO, (▲) 10 mol-% Cs⁺/MgO, (●) (5 mol-% Na⁺ + 5 mol-% Cs⁺)/MgO.

Table 2

Oxidative methylation of acetophenone (C₈H₈O) with methane over alkali promoted MgO. Reaction conditions: temperature 750°C, pressure atmospheric, amount of catalyst 0.5 g, total flow-rate 50 ml/min (NTP), P(CH₄):P(O₂):P(C₈H₈O):P(He) = 15.2:3.1:1:12.2. The results were obtained after 3 h of reaction

Catalyst (alkali in mol-%)	Conversion (%)			Selectivity (%)				C ₉ Yield (%) (PPN + IND)	
	C ₈ H ₈ O	O ₂	CH ₄	C ₉ H ₁₀ O (PNN) ^a	C ₉ H ₈ O (IND) ^b	Total C ₉ (PPN + IND)	SP ^c		CO _x (x = 1, 2)
10% Na ⁺ /MgO	27.8	97	7.1	14.1	7.8	21.9	28.9	40.9	6.1
10% Cs ⁺ /MgO	25.9	96	6.4	13.2	6.1	21.6	29.8	41.6	5.6
(5% Na ⁺ + 5% Cs ⁺)/MgO	31.0	98	8.0	18.6	8.5	27.1	26.8	37.2	8.4
MgO	8.8	91	1.8	8.8	4.8	13.6	27.6	53.0	1.2
Quartz wool	3.8	56	1.1	1.8	0.8	2.6	21.6	69.8	0.1

^a PPN = Propiophenone.

^b IND = 1-Indanone.

^c SP = side products include benzaldehyde, benzene, benzophenone, toluene, acetaldehyde, C₂, C₃ and C₄ hydrocarbons.

C₃ and C₄ hydrocarbons, and traces of unidentified products. The oxidative dehydrogenation product of propiophenone C₆H₅COCH=CH₂ is apparently unstable and undergoes cyclization to 1-indanone. Here again (Table 2), the bi-alkali promoted catalyst showed higher conversion and product selectivities than the corresponding mono-alkali promoted catalysts at the same alkali content of 10 mol-%. The pure MgO provided some C₉ product selectivity; however, this was lower than those over the alkali-promoted catalysts. Very small amounts of methylation prod-

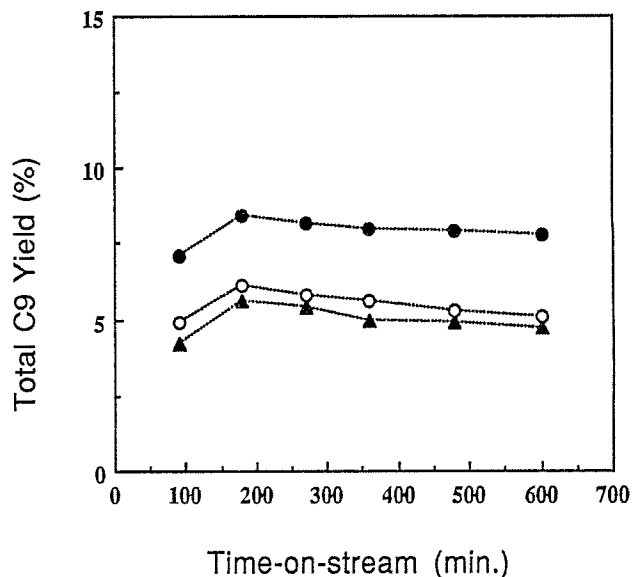


Fig. 2. The change in the C₉ product yield with time-on-stream in the oxidative methylation of acetophenone over alkali promoted MgO catalysts. Reaction conditions as in Table 2. Symbols as in Fig. 1.

ucts were observed with the reactor free of catalyst but containing the quartz wool plugs. In Fig. 2, the C₉ product yield is presented as a function of time-on-stream. There was no appreciable change in the product yield with time-on-stream, especially over the bialkali promoted catalyst.

The conversion and product yields of the oxidative methylation of diphenylmethane (C₆H₅CH₂C₆H₅) with methane over alkali promoted MgO catalysts are presented in Table 3. The primary products of this reaction were, 1,1-diphenylethane (C₆H₅CH(CH₃)C₆H₅), 1,1-diphenylethylene (C₆H₅C(CH₂)C₆H₅), carbon oxides (CO and CO₂) and water, with small amounts of benzene, toluene, ethyl-

Table 3

Oxidative methylation of diphenylmethane (C₁₃H₁₂) with methane over alkali promoted MgO. Reaction conditions: temperature 750°C, pressure atmospheric, amount of catalyst 0.5 g, total flow-rate 50 ml/min (NTP), P(CH₄):P(O₂):P(C₁₃H₁₂):P(He) = 21.6:4.7:1:17.3. The results were obtained after 3 h of reaction

Catalyst (alkali in mol-%)	Conversion (%)			Selectivity (%)					C ₁₄ Yield (%) (DPA + DPY)
	C ₁₃ H ₁₂	O ₂	CH ₄	C ₁₄ H ₁₄ (DPA) ^a	C ₁₄ H ₁₂ (DPY) ^b	Total C ₁₄ (DPA + DPY)	SP ^c	CO _x (x = 1, 2)	
10% Na ⁺ /MgO	33.1	98	7.3	11.9	14.1	26.0	26.8	38.6	8.6
10% Cs ⁺ /MgO	31.6	97	6.4	11.6	13.5	25.1	27.1	39.7	7.9
(5% Na ⁺ + 5% Cs ⁺)/MgO	37.2	98	8.2	15.4	17.1	32.5	23.4	36.2	12.1
MgO	15.4	91	2.3	7.8	5.8	13.6	26.6	51.8	2.1
Quartz wool	4.1	56	1.1	1.8	0.4	2.2	19.8	69.8	0.1

^a DPA = 1,1-diphenylethane.

^b DPY = 1,1-diphenylethylene.

^c SP = side products include benzene, toluene, ethylbenzene, styrene, bibenzyl, C₂, C₃ and C₄ hydrocarbons.

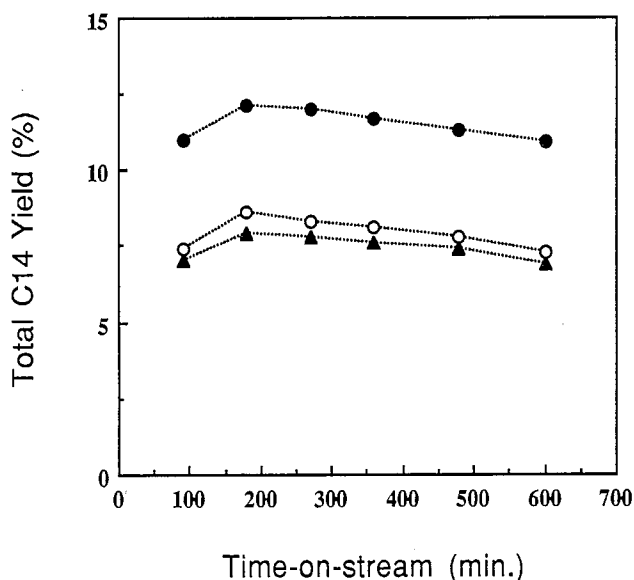


Fig. 3. The change in the C_{14} product yield with time-on-stream in the oxidative methylation of diphenylmethane over alkali promoted MgO catalysts. Reaction conditions as in Table 3. Symbols as in Fig. 1.

benzene, styrene, bibenzyl, C_2 , C_3 and C_4 hydrocarbons and some unidentified products. As noted for the other reactants, the product yield and the conversion are higher over the bi-alkali promoted catalyst than over the corresponding mono-alkali promoted catalysts. The activity and selectivity of the alkali promoted MgO catalysts are much higher than those of the unpromoted MgO. The empty reactor provided some small product yields, however, those yields are very small compared to those involving the catalysts. The C_{14} product yield is presented as a function of time-on-stream in Fig. 3. No substantial change in the product yield was observed during the 600 min time-on-stream study. A comparison of the bi-alkali-promoted system with the mono-alkali promoted ones shows that the stability of the former system is higher than those of the latter.

With all three substrates the conversion as well as the selectivities decrease, after an initial increase, with time-on-stream. However, the changes in the selectivities were small compared to that in conversion. Further, the variations in the conversions and selectivities are less significant over the bi-alkali promoted catalyst than over the mono-alkali promoted ones. This indicates that the stability with time-on-stream over the bi-alkali promoted system is higher than those over the mono-alkali promoted.

During the 600 min time-on-stream study, the drop in the product yield of the methylated compound over the bi-alkali promoted catalyst, after the initial small increase, was of about 3% for acetone, 7% for acetophenone and 10% for diphenylmethane. The higher decrease for the diphenylmethane is probably due to the deposition of some carbonaceous products which are normally expected with higher molecular weight hydrocarbons when used as reactants. Another disadvantage associated with higher molecular weight substrates is the formation of a larger number of side products. This results in smaller product selectivities.

The bialkali promoted MgO or CaO [14–17] catalysts are found to be more active and selective than the corresponding mono-alkali promoted systems in the oxidative coupling of methane or the oxidative methylation with methane. 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 X-ray photoelectron spectroscopy (XPS) measurements [14,15]. The enrichment is expected to be higher when the sizes of the promoting ions are very different, because then the surface can be more completely covered. This higher enrichment of the surface with alkali metals normally makes the catalyst surface more basic which in turn results in higher selectivity and conversion. This is in conformity with the earlier researchers observation that, by doping a catalyst with an alkali, the basicity of the surface is increased, which results in higher selectivity and conversion than that of the undoped catalyst [3,5]. Our results on the mono- or bialkali promoted MgO or CaO catalysts have indicated higher yields and better time-on-stream behavior for the combinations Li–Cs, Li–Rb and Na–Cs. However, in the case of Li and Rb containing catalysts, a substantial loss of these alkali metals during calcination and catalytic runs were noted from our atomic absorption spectroscopic measurements. For this reason, the bialkali combinations with Li and Rb cations exhibited lower performances than Na–Cs.

4. Conclusions

Acetone, acetophenone and diphenylmethane undergo oxidative methylation with methane over the alkali promoted magnesia catalysts, producing the corresponding methane coupling products. This work thus demonstrates that methane could be coupled to organic compounds containing reactive methyl groups. Further work is required in order to fully understand the mechanisms of these reactions and for the commercial viability of these processes.

The bialkali (5 mol-% Na–5 mol-% Cs)/MgO catalyst is superior to the mono-alkali promoted catalysts at the same alkali loading of 10 mol-%.

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