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Green chemistry perspectives of methane conversion *via* oxidative methylation of aromatics over zeolite catalysts†

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Methane gas is known to be the most destructive greenhouse gas. The current world reserves of natural gas, which contains mainly methane, are also still underutilized due to high transportation costs. Thus, considerable interest is presently shown in conversion of methane to transportable liquid fuels and chemicals of importance to the petrochemical industry. The catalytic methylation of aromatics is one possible new route for converting methane to more valuable higher hydrocarbons. This paper provides a general overview of the recent work that we and other researchers have done on the utilisation of methane for catalytic methylation of aromatic compounds and for direct coal liquefaction for the production of liquid hydrocarbons. In particular, the paper presents a detailed description of more recent substantial experimental evidence that we have provided for the requirement of oxygen as a stoichiometry reactant for benzene methylation with methane over moderately acidic zeolite catalysts. The reaction, which has been termed ''oxidative methylation'', was thus postulated to involve a two-step mechanism involving intermediate methanol formation by methane partial oxidation, followed by benzene methylation with methanol in the second step. However, strongly acidic zeolites can cause cracking of benzene to yield methylated products in the absence of oxygen. The participation of methane and oxygen, and the effective use of zeolite catalysts in this methylation reaction definitely have some positive green chemistry implications. Thus, the results of these previous studies are also discussed in this review in light of the principles and tools of green chemistry. Various metrics were used to evaluate the greenness, cost-effectiveness, and material and energy efficiency of the oxidative methylation reaction.

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1 Introduction

Methane gas has been identified to be the most destructive greenhouse gas.[1] The gas is also the major constituent of natural gas, the current world reserves of which are still underutilised due to high costs of transportation, especially from the remote areas of Asia, Siberia, Western Canada and offshore reservoirs of Australia where they are located. Hence, considerable interest is presently shown in the conversion of methane to transportable liquid fuels and chemicals of importance to petrochemical industry in addition to its previous sole use for heating purposes by combustion. One problem with methane conversion is the stability of the methane molecule, with a C–H bond energy of 439 kJ mol^{-1}, which makes it resistant to many reactants.[2] Hence, considerable efforts have been made by researchers on the development of catalytic processes for activation of methane. The conventional catalytic technology for the conversion of methane to liquid fuels and feedstocks involves a two-step process in which methane is first converted to synthesis gas by steam reforming (eqn (1)), CO_2 reforming (eqn (2)), or partial oxidation (eqn (3)),[3] followed by either Fischer–Tropsch synthesis of hydrocarbons or methanol synthesis and conversion to hydrocarbons.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \ (\Delta H^0_{298K} = +206 \text{ kJ mol}^{-1})^4 \quad (1)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \ (\Delta H^0_{298K} = +247 \text{ kJ mol}^{-1})^{4,5} \quad (2)$$

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$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \ (\Delta H^0_{298K} = -36 \text{ kJ mol}^{-1})^6 \quad (3)$$

The catalytic steam reforming process is conducted over a supported nickel catalyst and is an established technology.[7] The water–gas shift reaction (eqn (4)) which is used to adjust the H_2/CO ratio to suit the subsequent use to which the synthesis gas is to be put is also an established technology:

$$CO + H_2O \rightarrow CO_2 + H_2 \ (\Delta H^0_{298K} = -41 \text{ kJ mol}^{-1})^4 \quad (4)$$

The overall reforming reaction is highly endothermic and consumes a considerable amount of energy. The process is generally regarded as being inefficient and very costly, constituting about 70% of the investments in a methanol plant.[8]

The Fischer–Tropsch synthesis represented by eqn (5) is essentially an oligomerisation/polymerisation process involving the conversion of the synthesis gas to higher hydrocarbons covering a fairly wide range of molecular weights. Since the hydrocarbons produced are mainly aliphatic in nature and usually without extensive chain branching, further processing is required if a high-octane gasoline is the desired end product.

$$n\text{CO} + 2n\text{H}_2 \rightarrow (\text{–CH}_2)_n + n\text{H}_2\text{O} \quad (\Delta H^0_{298K} = -165 \text{ kJ mol}^{-1})^9 \quad (5)$$

The classical Fischer–Tropsch process is conducted over an iron catalyst and is a developed technology.[10]

The conversion of synthesis gas to methanol for subsequent conversion of the methanol to hydrocarbons *via* the methanol-to-gasoline (MTG) Mobil Technology process is also an established process represented by the following reactions:

$$CO + 2H_2 \rightarrow CH_3OH_{(g)} \ (\Delta H^0_{298K} = -90.8 \text{ kJ mol}^{-1})^{11,12} \quad (6)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH_{(g)} + H_2O \quad (\Delta H^0_{298K} = -49.5 \text{ kJ mol}^{-1})^{11,12} \quad (7)$$

The modern low-pressure methanol synthesis technology developed by ICI involves the passage of a gas mixture containing H_2, CO and CO_2 over a catalyst containing Cu, ZnO and Al_2O_3 at temperature of about 250–300 °C and 50–100 atm pressure.[13] The MTG process is conducted over HZSM-5 catalyst, and it is generally agreed that the reaction is Brønsted acid catalysed, and proceeds first to the formation of C_2 and C_3 olefins which undergo chain length by step-wise chain growth and by oligomerisation followed by cyclisation and aromatisation to give aromatics in the C_6–C_{10} range.[13]

Other approaches of catalytic methane conversion that have been extensively investigated but not yet implemented on an industrial scale include catalytic partial oxidation of methane to methanol (eqn (8)) and oxidative coupling to C_2 hydrocarbons. The direct partial oxidation of methane to methanol would be a highly desirable alternative to the synthesis gas route since it is exothermic, and because, in principle, a single step process would be technically simpler, particularly in relation to the efficiency of heat recovery upon which the synthesis gas route depends for its economic viability. Unfortunately, the complete or 'deep' oxidation to CO and CO_2 (eqn (10) and (11)) is thermodynamically even more favourable so that it is necessary to preserve the valuable primary oxygenated product which can be done by either product removal or suppression of secondary reactions:[11,12]

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CH_3OH_{(g)} \ (\Delta H^0_{298K} = -126.4 \text{ kJ mol}^{-1}) \quad (8)$$

$$CH_4 + O_2 \rightarrow HCHO_{(g)} + H_2O_{(g)} \quad (\Delta H^0_{298K} = -276 \text{ kJ mol}^{-1}) \quad (9)$$

$$CH_4 + O_2 \rightarrow CO + 2H_2O_{(g)} \quad (\Delta H^0_{298K} = -519.6 \text{ kJ mol}^{-1}) \quad (10)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(g)} \quad (\Delta H^0_{298K} = -802.6 \text{ kJ mol}^{-1}) \quad (11)$$

Several reviews[3–6,12–20] on these processes and other methane catalytic conversion processes have been published.

One possible new route for the utilisation of methane derived from natural gas or other sources for conversion to more valuable higher hydrocarbons is the methylation of aromatic hydrocarbons. This route has been the subject of some recent investigations.[21–32] For example, the direct methylation of naphthalene, toluene and phenol with methane over aluminophosphate molecular sieves in a high pressure batch reactor has been demonstrated.[21,22] More recent batch reaction investigations[25,26] have also revealed the incorporation of methane in the presence of Cu-beta, H-beta and CuZSM-5 into a variety of organic substrates (*eg.* benzene, toluene, phenol) which model petroleum, coal and liquefaction residue structures. The utilisation of methane in this way is one of the possible uses of natural gas in the petrochemical industry for the production of chemicals of industrial importance. Methane can also be used in such methylation reactions as a hydrogen-rich reagent, in place of the more expensive hydrogen that is currently used, for the production of liquid hydrocarbons by direct coal liquefaction at pyrolysis temperatures. For example, Long *et al.*[33] have demonstrated the reactivity of methane with a range of coals in the temperature range of 350–400 °C and pressure range of 6.0–8.3 MPa over aluminophosphate or zeolite catalysts. However, in contrast to these previous findings, other workers have also reported that methane did not take part in forming methylated aromatic products,[24] an issue that the results of our investigations have now resolved. The direct methylation of aromatics with methane (represented by eqn (12) for benzene) is not thermodynamically feasible under normal conditions, but significant yields of methylated products are feasible if the reaction is carried out in the presence of a large excess of methane. Thus, the reactions have often been carried out under high methane pressures (up to 6.9 MPa or 1000 psi), although some investigators have reported high yields of methylated products at only 1 atm and at temperatures as low as 100 °C using superacid catalysts.[34]

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(ΔG = +43.2 & +42.2 kJ/mol at 298 & 673 K, respectively)

(12)

We had previously carried out a series of studies to address the challenges of thermodynamic barrier and inconsistency in previous results with respect to methane participation. These studies were also conducted to investigate the possible role of oxygen in the reaction and to develop better catalysts for methane activation. This paper provides a general overview of such investigations and those of other researchers on the use of methane for catalytic methylation of model aromatic compounds and for direct liquefaction of coal for the production of liquid hydrocarbons. In particular, we present here a detailed discussion of recent substantial experimental evidence that we have provided for the requirement of oxygen as a stoichiometric reactant for benzene methylation with methane over moderately acidic zeolite catalysts. Such an oxidative methylation reaction was postulated to involve a 2-step mechanism involving intermediate methanol formation by methane partial oxidation followed by benzene methylation with methanol in the second step. However, strongly acidic zeolites were found to cause cracking of benzene to yield methylated products in the absence of oxygen. These results have now resolved the lack of agreement in previous studies. Furthermore, our findings that both methane and oxygen participated in the reaction and zeolites were effectively used as catalysts in the methylation reaction definitely have some green chemistry implications. Thus, we also present in this paper a discussion of these previous studies of the aromatics oxidative methylation reaction in light of the principles and tools of green chemistry.

2 Utilisation of methane in catalytic methylation of aromatics

2.1 Direct catalytic methylation of aromatics with methane

As already mentioned, the activation of methane for direct methylation of hydrocarbons is one possible way of utilising methane derived from natural gas or other sources for conversion into more valuable higher hydrocarbons. In this regard, Long and co-workers[21,22] have previously demonstrated that substituted aluminophosphate molecular sieves catalysed the methylation of naphthalene, toluene and phenol in a batch reactor at 400 °C and 6.9 MPa methane pressure. These workers then subsequently confirmed using a $^{13}CH_4$ isotropic tracer experiment that the methyl groups in the substituted naphthalene products were derived mainly from methane, thereby indicating direct methylation of naphthalene.[23] Thus, for example, the GC-mass spectrometric analysis of the products of the reaction using $^{13}CH_4$ showed that the methylnaphthalene formed from naphthalene contained principally one ^{13}C atom and the dimethylnaphthalene contained two ^{13}C atoms per molecule. A further confirmation was also obtained from ^{1}H NMR spectra of the products, which indicated an estimate of 73% ^{13}C in the methyl groups of the products of the $^{13}CH_4$ experiment. Long *et al.*[25] have also demonstrated in a later $^{13}CH_4$ isotopic tracer study that the reaction of benzene with methane over H-beta and Cu-beta at 400 °C and 5.5 MPa methane-^{13}C pressure yielded toluene and xylene products containing substantially methyl-^{13}C substituents. This then confirmed that direct methylation of benzene with methane was possible under their reaction conditions in a batch reactor. However, these workers also proposed a second mechanism in which the methylated products are formed by fragmentation and rearrangement of benzene rather than from the reactions of methane itself. It was then suggested that this other mechanism would be favoured by a more acidic zeolite catalyst, since acidity generally promotes cracking and coking of hydrocarbons. In a later investigation by Long *et al.*,[26] two mechanisms were also identified for the conversion of methane by a reaction with a wide range of organic substrates (*e.g.* benzene, toluene, phenol *etc.*) over Cu-beta, H-beta and CuZSM-5 catalysts at 350–450 °C and 3.5–9 MPa pressures. According to these workers, one mechanism involved direct methylation by addition of methyl groups while the other involved a disproportionation process probably resulting in carbon deposition.

In contrast to these findings, earlier $^{13}CH_4$ studies[35,36] of the methylation of benzene and some other hydrocarbons with methane over nickel on silica and alumina catalysts showed that the methyl group was largely derived from sources other than methane gas. Carbonaceous species were thought to supply part of the carbon for methylation. A more recent $^{13}CH_4$ isotopic tracer investigation by Lunsford and co-workers[24] also failed to reveal the presence of any detectable ^{13}C in the methylated products of the methylation of benzene over H-beta catalyst in a flow reactor at 400 °C and 4.8 MPa pressure. They then concluded that benzene served as the sole source of carbon in all of the observed products under their reaction conditions.[24] Thus, it appears that there was lack of agreement in previous reported studies with regard to the participation of methane for the supply of methyl groups in the methylation reactions.

2.2 Oxidative methylation of benzene with methane over zeolite catalysts

The question of whether or not methane can be activated over zeolite catalysts to methylate aromatics is an important one to answer in the context of new routes for the utilisation of methane derived from natural gas. Adebajo *et al.* have therefore carried out a series of investigations[27–29,32,37] on the methylation of benzene with methane over zeolite catalysts that have now resolved the lack of consistency in the previous reported studies as to the actual source of methyl groups in the methylation reactions. A factor not considered in previous work that was looked at in these investigations is the possible role of oxygen in the autoclave during the loading of reactants. These workers have now been able to demonstrate that the presence of oxygen is actually required for the production of methylated products in the methylation of benzene with methane at 400 °C over zeolite catalysts in a high-pressure batch reactor. This is illustrated in Fig. 1 for experiments with

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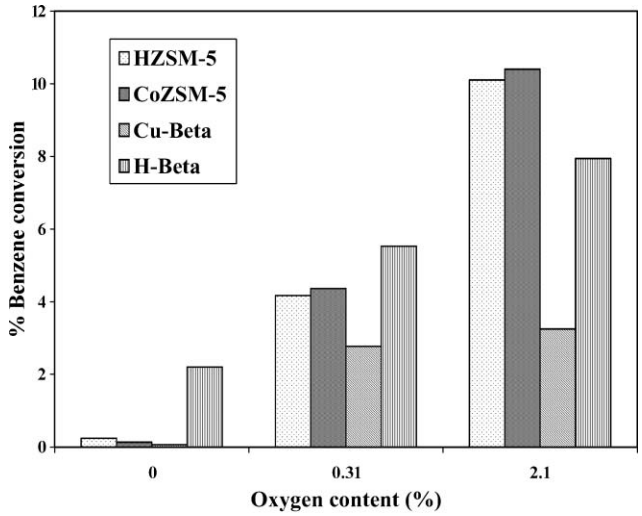

Fig. 1 Variation of benzene conversion with oxygen content for the methylation of benzene with methane in a batch reactor at 400 °C and 6.9 MPa pressure for 4 h.[27,28]

four different catalysts. It is shown clearly in Fig. 1 that only in the case of zeolite H-beta is there a significant benzene conversion in the absence of oxygen. Fig. 1 also shows that there is an increase in conversion with an increase in the residual oxygen content for all the catalysts.

Experiments with $^{13}CH_4$ also confirmed the earlier reports that methyl groups in the toluene and xylene products originate at least in part from methane. This is illustrated in Table 1 and Fig. 2 and 3. The results of GC/MS analysis of reaction products of one $^{13}CH_4$ experiment shown in Table 1 indicate that the toluene product increased in molecular weight by one mass unit on substitution of $^{13}CH_4$ for $^{12}CH_4$, while *p*-, *m*-, and *o*-xylenes each increased in molecular weight by two mass units. These results, therefore, confirm that additional C atom(s) in the reaction products originated from methane itself. Fig. 2 shows the ^{13}C solution NMR spectrum of the reaction products of the $^{13}CH_4$ experiment. This

Table 1 Relative peak intensities in GC/MS analysis of products of reaction of $^{13}CH_4$ with benzene over Co-ZSM-5 at 400 °C and 7.1 MPa for 4 h

Product	Methane-^{12}C reaction	Methane-^{13}C reaction
Toluene		
m/z = 90	—	12.9
m/z = 91	105.8	26.9
m/z = 92	100.0	108.4
m/z = 93	13.6	100.0
m/z = 94	—	8.4
p/m-xylene		
m/z = 105	17.5	135.7
m/z = 106	100.0	57.1
m/z = 107	7.5	78.6
m/z = 108	—	100.0
m/z = 109	—	—
o-xylene		
m/z = 105	43.3	52.9
m/z = 106	100.0	29.4
m/z = 107	7.5	50.0
m/z = 108	—	100.0
m/z = 109	—	—

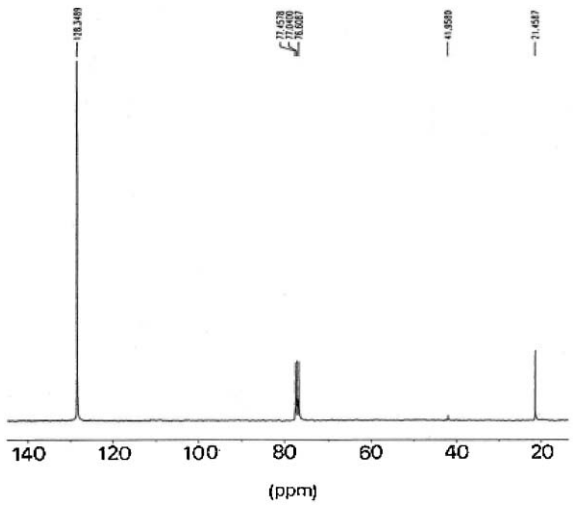

Fig. 2 ^{13}C solution NMR spectrum of $CDCl_3$ solution of products of reaction of $^{13}CH_4$ with benzene over CoZSM-5 at 400 °C and 7.1 MPa pressure for 4 h.

spectrum shows a strong signal at 128.3 ppm which is primarily due to benzene. The signal normally observed at 125.3 ppm due to the aromatic toluene carbons alone is not visible in Fig. 2 due to the relatively small amount of toluene produced in the $^{13}CH_4$ experiment. Nevertheless, the signal at about 21.5 ppm assigned to methyl groups of toluene is very strong implying that the isotopic abundance in the methyl group is at least an order of magnitude above that of the aromatic nucleus. Thus, Fig. 2 indicates that ^{13}C from the $^{13}CH_4$ was incorporated into the methylated reaction products. Fig. 3 shows the methyl region of the ^{1}H NMR spectrum of the reaction products of the $^{13}CH_4$ experiment. The $^{13}C/^{12}C$ ratio in the methyl groups in the sample can be estimated by comparison of the J-coupled methyl resonance of $^{1}H–^{13}C$ (satellite peaks on the left and right) and the unsplit methyl resonance of $^{1}H–^{12}C$ (centre signal). From the intensities of these peaks, it was estimated that 92% of the methyl carbon originated from the methane-^{13}C gas when Co-ZSM-5 was used as catalyst. It is therefore concluded that

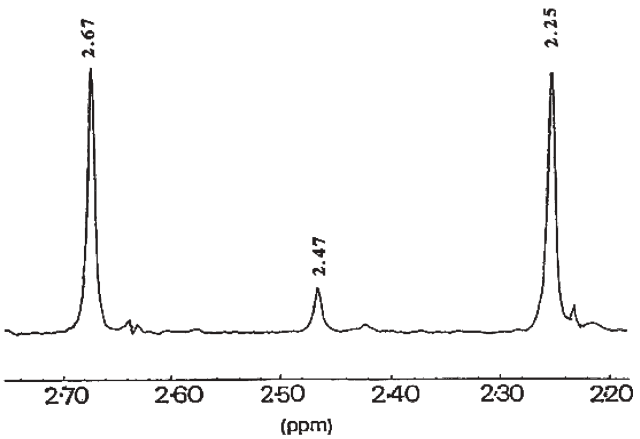

Fig. 3 ^{1}H solution NMR spectrum of $CDCl_3$ solution of products of reaction of $^{13}CH_4$ with benzene over CoZSM-5 at 400 °C and 7.1 MPa pressure for 4 h.

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Table 2 Conversion of benzene and selectivity to products for the reaction of benzene with (1) methane + air, (2) under nitrogen and (3) under hydrogen[32]

1. Methane + air[a]

		Selectivity to products (%)		
Catalyst	Conversion (%)	Toluene	Ethylbenzene	Xylenes
None	0.77	33.3	10.0	28.9
HZSM-5	9.32	65.7	17.4	15.5
CoZSM-5	8.14	48.1	31.5	18.5
MnZSM-5	8.46	40.6	40.6	16.4
CuZSM-5	8.02	41.4	37.7	18.5
NaZSM-5	7.93	51.4	28.8	18.2

2. Nitrogen[b]

		Selectivity to products (%)		
Catalyst	Conversion (%)	Toluene	Ethylbenzene	Xylenes
HZSM-5	0.08	65.4	34.6	—
CoZSM-5	0.28	63.0	28.1	8.88
MnZSM-5	0.14	61.1	38.9	—
CuZSM-5	0.07	66.0	34.0	—
NaZSM-5	0.18	54.2	33.2	12.6

3. Hydrogen[c]

		Selectivity to products (%)		
Catalyst	Conversion (%)	Toluene	Ethylbenzene	Xylenes
HZSM-5	1.25	65.1	22.6	12.3
CoZSM-5	1.06	50.8	37.1	9.62
MnZSM-5	0.76	46.8	36.5	16.6
CuZSM-5	0.30	36.9	50.5	5.61
NaZSM-5	0.29	60.2	39.8	—

[a] 400 °C, 6.9 MPa CP grade methane, 4 h reaction time, no removal of residual air. [b] 400 °C, 6.9 MPa nitrogen, 4 h reaction time, no removal of residual air (*i.e.* same reaction conditions as for methane, except that methane is replaced with nitrogen). [c] Same reaction conditions as for methane except that residual air is removed and methane is replaced with hydrogen.

the methane unequivocally provided the methyl groups incorporated into the substituted aromatic products. As shown in Table 2, blank experiments with catalysts but in which methane was replaced with 6.9 MPa nitrogen have further demonstrated the participation of methane in the reaction to produce methylated products.[32] Table 2 also demonstrates the importance of the presence of zeolite catalysts for converting benzene to methylated products, since blank runs without a catalyst yielded only 0.8% benzene conversion compared with 8–9% conversions obtained when catalysts were included.

The participation of methane in the reaction was also shown to be limited by the amount of oxygen present in the reaction system.[32] Adebajo *et al.* also observed in their investigations that when catalyst was excluded and the batch reactor was flushed with oxygen prior to adding methane, methanol was the major product obtained (about 86% selectivity).[28] Furthermore, the methanol was not detected in the presence of zeolite catalysts when oxygen was introduced into the reactor. This suggests that all of the methanol reactant, being more reactive than the initial methane reactant, was consumed to form methylated products over the catalysts. Reactions in the presence of catalyst but at the exclusion of benzene yielded significant amounts of aromatic hydrocarbons (mainly

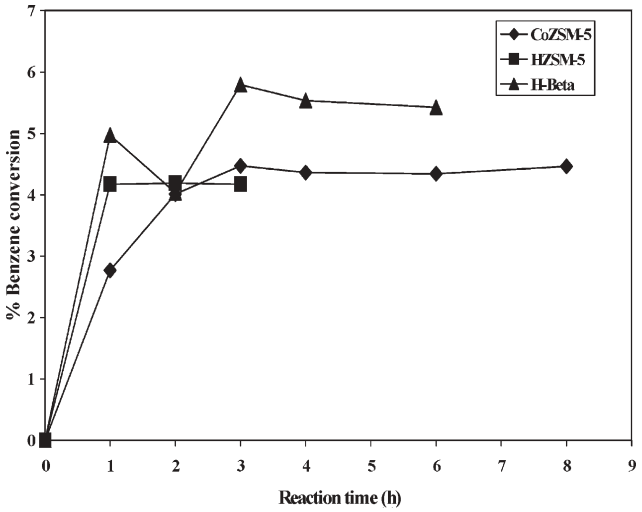

Fig. 4 Variation of benzene conversion with reaction time for the methylation of benzene with methane without removal of residual air in batch reactor at 400 °C and 6.9 MPa pressure.[28]

benzene, toluene and xylenes) that are expected for methanol conversion over acid catalysts. These workers have shown that such methanol-to-aromatics conversion contributes significantly to the benzene methylation reaction.[31]

Adebajo *et al.* further indicated that the addition of methanol to the batch reactor containing benzene, methane and catalyst which had been totally purged of oxygen gave conversions and product selectivities similar to those found in the presence of oxygen.[27,28] For example, addition of 1.2 mol% methanol gave 0.75% conversion of benzene to toluene and 10.4 mol% methanol gave 5.6% conversion of benzene. It has been demonstrated too that there is no significant effect on benzene conversion and product selectivity on increasing the reaction time beyond 2 h.[27,28] This is illustrated in Fig. 4 for benzene conversion. This cannot be due to catalyst poisoning (*e.g.* by coke deposition), since it has been shown that catalysts recovered from the reactor could be reused without loss of performance (Table 3).[38] The XRD patterns of the zeolites catalysts were also observed to remain unchanged after reaction, as illustrated in Fig. 5 for H-beta. The observation can rather be attributed to the reaction being limited by the amount of oxygen in the reactor, which has already been shown to be the case.[32]

Thus, on the basis of these observations reported by Adebajo *et al.*, the reaction was postulated to go *via* a two-step

Table 3 Comparison of fresh with used ZSM-5 catalysts for methane reaction with benzene in the presence of residual air at 400 °C and 6.9 MPa pressure[38]

	Benzene conversion	Selectivity to products (%)		
Reaction time/catalyst	(%)	Toluene	Ethylbenzene	Xylenes
2 Hours				
Fresh HZSM-5	4.19	92.9	4.25	2.86
Used HZSM-5	4.01	91.7	4.34	3.98
4 Hours				
Fresh CoZSM-5	4.36	91.4	3.85	4.75
Used CoZSM-5	3.39	94.1	2.65	3.30

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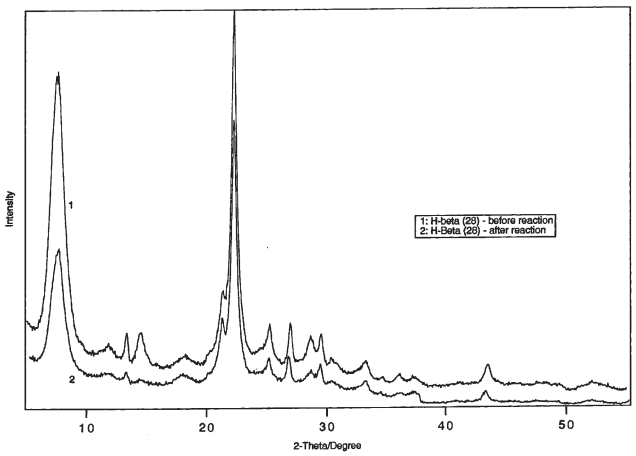

Fig. 5 XRD patterns of H-beta before and after reaction.[38]

mechanism involving the intermediate formation of methanol by partial oxidation of methane followed by the methylation of benzene with methanol in the second step. The two steps of the reaction are therefore represented by eqn (13) and (14) as follows:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CH_3OH \quad (13)$$

$$CH_3OH + C_6H_6 \rightarrow C_6H_5CH_3 + H_2O \quad (14)$$

It then follows that the overall reaction is given by eqn (15):

$$C_6H_6 + CH_4 + \tfrac{1}{2}O_2 \rightarrow C_6H_5CH_3 + H_2O \quad (15)$$

In support of this mechanism, the performance of the catalysts for both benzene methylation with methanol (low pressure flow reaction) and with methane in the presence of oxygen (high pressure batch reaction) have subsequently been demonstrated to show excellent correlation.[37] However, in the case of H-beta that exhibits strong acidity, it was shown that methyl aromatics could be formed in the absence of oxygen. This is consistent with an earlier report by Lunsford *et al.*[24] that these products are formed from the cracking of benzene over the acidic zeolite. The zeolites provide the small number acid sites of moderate strength that are necessary for the reaction.[27,28]

Adebajo *et al.*[29] have also previously shown that the purity of methane used in the methylation of benzene over zeolite catalysts is critical in determining conversion and product selectivities. Trace amounts of ethylene impurities in the methane used was found to enhance benzene conversions and selectivities to ethylbenzene. However, methane containing ethane impurities yielded negligible benzene conversion in the absence of oxygen over CoZSM-5 catalyst while a much higher conversion was obtained over H-beta due mainly to cracking of benzene.[24] These observations are illustrated in Tables 4 and 5.

It therefore appears from the findings reported by Adebajo and co-workers that the zeolites that were used in their series of investigations are not capable of directly activating methane under the relatively mild conditions that they employed. The function of the zeolite catalysts in the high pressure batch reactor was also reported to be the provision of acid sites of moderate strength to catalyse the methylation of benzene (or other aromatics) by methanol.[27,28] Strong acidity, such as that exhibited by zeolite H-beta, causes cracking of the aromatics and should therefore be avoided.[24,27,28]

Table 4 Effect of the purity of methane on methylation of benzene[29] under standard conditions[a]

	Type of methane used[b]	HZSM-5	CoZSM-5
Benzene conversion (%)	CP grade	9.32	8.14
	UHP grade	4.17	4.36
Selectivity to toluene (%)	CP grade	65.7	48.1
	UHP grade	93.0	91.4
Selectivity to ethylbenzene (%)	CP grade	17.4	31.5
	UHP grade	4.05	3.85
Toluene/ethylbenzene ratio	CP grade	3.78	1.53
	UHP grade	23.0	23.7

[a] Reaction conditions: 400 °C, 6.9 MPa methane, 4 h reaction time, no removal of residual air. [b] CP methane is chemically pure grade (>99.0% pure) and UHP methane is ultrahigh purity grade (>99.97% pure).

Table 5 Effect of adding ethane and ethylene to the methane used in the methylation of benzene over CoZSM-5 catalyst[29] under standard conditions[a]

	UHP methane + 2.1% ethane[b] (nil O_2)		UHP methane + 2.1% ethylene[b] (nil O_2)	
	CoZSM-5	H-beta	CoZSM-5	H-beta
Benzene conversion (%)	0.60	2.76	28.9	35.5
Selectivity to toluene (%)	66.3	87.7	20.9	23.8
Selectivity to ethylbenzene (%)	33.7	12.3	59.7	62.7
Toluene/ethylbenzene ratio	1.97	7.13	0.35	0.38

[a] Reaction conditions: 400 °C, 6.9 MPa methane, 4 h reaction time, removal of residual air. [b] Ethane/benzene and ethylene/benzene molar ratio in the feed 0.64.

However, Adebajo *et al.* have been able to convincingly demonstrate that *in situ* methylation using methane can be achieved by combining methanol synthesis by partial oxidation of the methane with methylation of aromatics with the methanol intermediate. This concept is very similar to the earlier demonstration by Gesser and co-workers[39] that methane partial oxidation could be combined with methanol conversion to gasoline in a two-stage continuous flow reactor.

2.3 Thermodynamics of oxidative methylation of benzene with methane

Fig. 6 shows the plots of the free energies and heats of reaction (ΔG and ΔH), and ln K against temperature for the oxidative benzene methylation reaction (eqn 15). The regression equations for the ΔG and ΔH plots are as follows:

$$\Delta G = 0.045T - 198.557 \qquad r = 1.000 \quad (16)$$

$$\Delta H = -2.714 \times 10^{-6}T^2 + 7.228 \times 10^{-3}T - 202.225 \qquad r = 0.9995 \quad (17)$$

Unlike the direct methylation reaction (eqn (12)), Fig. 6 indicates clearly that the overall oxidative methylation reaction

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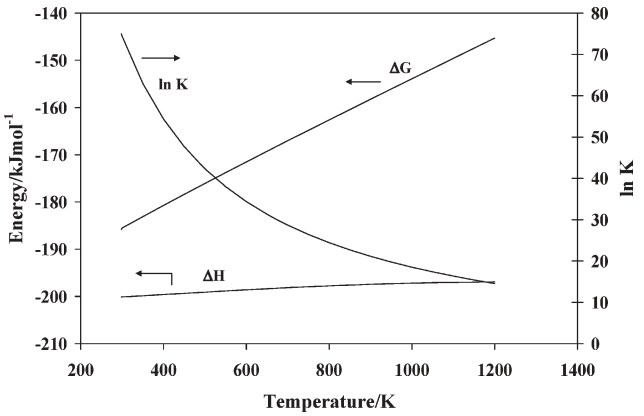


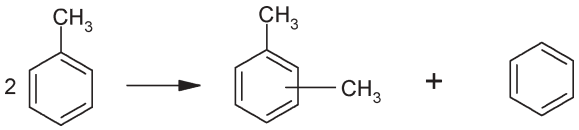
Fig. 6 Plots of ΔG, ΔH and ln K against temperature for the oxidative benzene methylation eqn (15).

is thermodynamically feasible with highly negative ΔG and ΔH over the temperature range from ambient to 1200 K. Both ΔG and ΔH are shown in Fig. 6 to increase with increase in temperature. Fig. 6 also shows that the equilibrium constants of the reaction over the whole temperature range are very large due to the highly negative free energies of reaction. 100% benzene conversion is therefore predicted for the whole temperature range. The equilibrium constant is also shown to decrease with an increase in temperature, which is consistent with the exothermic nature of the reaction. Thus, it is clear from the thermodynamic data that the oxidative benzene methylation reaction is much more feasible, and therefore more likely to occur, than the direct non-oxidative methylation eqn (12). It is therefore possible to conduct the oxidative reaction using air or O_2 at atmospheric pressure and much lower temperatures. This is an area for further investigation.

2.4 Oxidative methylation of toluene with methane

In view of the two-step mechanism *via* intermediate formation of methanol proposed by Adebajo *et al.*[27–29,32,37] for the oxidative methylation of benzene with methane over acidic zeolites in a high-pressure batch reactor, a preliminary investigation was carried out by these workers[30] on the reaction of toluene with methane over acidic ZSM-5 catalysts in a batch reactor containing residual air to determine the actual contribution of direct methylation (*via* intermediate methanol formation) to the observed reaction products. The reactions were carried out at 400 °C and 6.9 MPa pressure. The major reaction products obtained by these workers were benzene and xylenes. Smaller amounts of ethylbenzene, trimethylbenzene and other higher aromatics were also produced. Over acidic catalysts, the conversion of toluene can, in principle, occur through two different reaction pathways: methylation by methane *via* methanol (as in the case of benzene methylation) and disproportionation, as shown in eqn (17) and (18):

(17)



(18)

The formation of the methanol by partial oxidation of methane is shown in eqn (13). Both pathways produce xylene products, but only disproportionation produces benzene. Further methylation of xylenes will produce C_9 and higher aromatics, but such molecules may also be formed by disproportionation of xylenes. The selectivity data in Table 6 show that the disproportionation of toluene is a significant pathway over all the zeolite catalysts when the reaction was carried out in the presence of methane–air mixtures since benzene is a major product of the reaction. In an attempt to separate the methylation and disproportionation pathways, Adebajo *et al.* carried out the reaction of toluene over the same catalysts in the presence of nitrogen alone. Under these conditions, disproportionation is the only possible pathway. Their results shown in Fig. 7 and Table 6 indicate that disproportionation is the major pathway followed over the zeolites containing a greater number of acid sites [*i.e.* HZSM-5 (SiO_2/Al_2O_3 = 35), CoZSM-5 and MnZSM-5]. This is because toluene conversion and product selectivities are similar in both methane–air and nitrogen mixtures over these catalysts, although over the CoZSM-5 and MnZSM-5, the yields of C_9

Table 6 [28,30] Conversion of toluene and selectivity to products for the reaction of toluene (a) with methane + air, (b) under nitrogen and (c) under hydrogen

(a) Methane + air[a]

Catalyst	Conversion (%)	Selectivity (%)			
		Benzene	Ethylbenzene	Xylenes	C_{9+} aromatics
CuZSM-5	8.42	33.8	3.69	17.5	44.9
MnZSM-5	14.9	52.1	2.95	33.5	11.4
Co-ZSM-5	14.8	40.9	3.64	42.1	13.3
NaZSM-5	15.0	46.2	3.59	34.9	15.4
HZSM-5[b]	7.41	37.5	3.44	23.0	36.0
HZSM-5	33.0	54.3	2.27	39.5	3.95

(b) Nitrogen[c]

Catalyst	Conversion (%)	Selectivity (%)			
		Benzene	Ethylbenzene	Xylenes	C_{9+} aromatics
CuZSM-5	4.48	85.9	1.19	12.1	0.78
MnZSM-5	16.0	60.2	1.09	35.7	2.97
Co-ZSM-5	17.6	63.8	0.88	33.6	1.70
NaZSM-5	3.11	72.7	2.00	22.7	2.62
HZSM-5[b]	4.66	76.2	1.87	19.5	2.46
HZSM-5	36.0	58.9	0.86	38.1	2.13

(c) Hydrogen[d]

Catalyst	Conversion (%)	Selectivity (%)			
		Benzene	Ethylbenzene	Xylenes	C_{9+} aromatics
CuZSM-5	7.00	52.8	0.38	45.5	1.29
NaZSM-5	10.3	57.8	0.51	40.4	4.15

[a] 400 °C, 6.9 MPa methane, 4 h reaction time, no removal of residual air. [b] SiO_2/Al_2O_3 ratio for this catalyst is 140. [c] Same reaction conditions as for methane, except that methane is replaced with nitrogen. [d] Same reaction conditions as for methane, except that methane is replaced with hydrogen.

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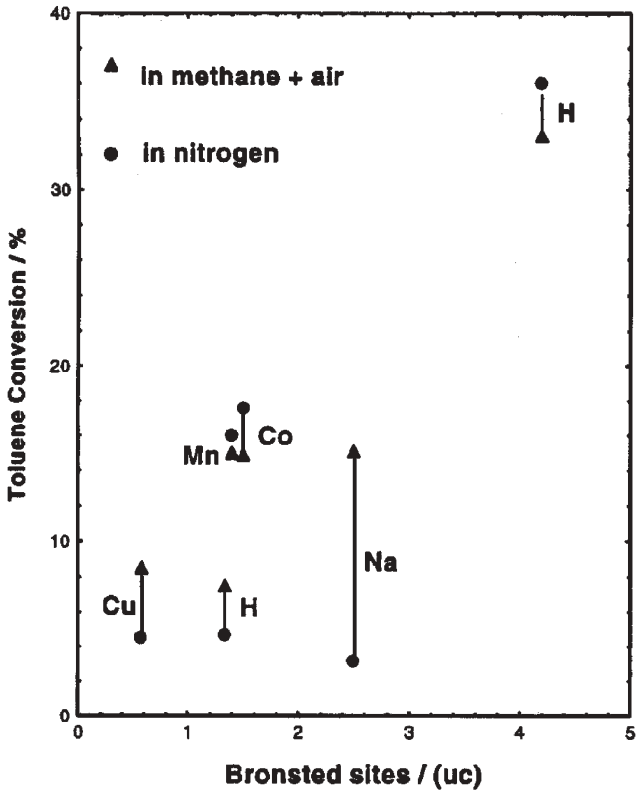
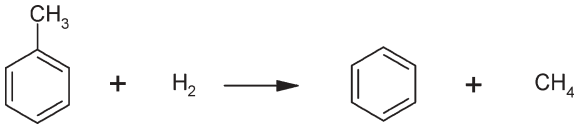


Fig. 7 Plots of toluene conversion against Brønsted acid concentration for reactions carried out in methane–air and in nitrogen.[30]

and higher aromatics are slightly enhanced in methane–air mixtures. The contribution from disproportionation is reduced and the methylation reaction is enhanced over NaZSM-5 that contains an alkali metal cation and over CuZSM-5 and HZSM-5 that have fewer acid sites. Thus, there are significant differences in the conversions and product selectivities in nitrogen and methane–air mixtures over these catalysts, as shown in Fig. 7 and Table 6.

Adebajo *et al.*[30] therefore concluded that in the reaction of toluene with methane in the presence of air, the relative contributions of the methylation and disproportionation reactions depend on the concentrations and strengths of acid sites in the zeolite catalysts used. Disproportionation appears to be reduced and methylation significantly enhanced over catalysts containing fewer acid sites and alkali metal cations. Since the metal-substituted aluminophosphate catalysts employed in the study of toluene methylation reported in earlier investigation[22] do not contain strong acid sites, it is likely that the xylenes observed in that work result from the methylation reaction rather than disproportionation. However, it was then suggested by these workers[30] that disproportionation must always be considered as a possible reaction pathway in reactions of all aromatic compounds with methane under these conditions in the presence of catalysts containing acid sites.

Adebajo and co-workers[28] have also observed considerable toluene conversions over CuZSM-5 and NaZSM-5 when methane was replaced with hydrogen as shown in Table 6. This suggests that the conversion of toluene also involved hydrodealkylation and hydrocracking reactions in addition to the disproportionation reaction. The hydrodealkylation reaction involves reaction of the toluene with hydrogen to produce benzene and methane as shown in eqn (19):



(19)

Huang and Howe[40] had also previously reported that the toluene reaction over Mo-exchanged ZSM-5 when hydrogen was used as the carrier gas consisted mainly of disproportionation, hydrodealkylation and hydrocracking reactions. However, the toluene conversions obtained from the hydrogen runs over CuZSM-5 and particularly over NaZSM-5 are lower to some extent than the values obtained from the methane runs (Table 6). Therefore, a certain degree of methylation by some reaction with methane might have also occurred in addition to the hydrodealkylation reaction. It was therefore concluded by Adebajo and co-workers that the methylation of toluene with methane in the presence of oxygen over zeolite catalysts is complicated by extensive disproportionation, hydrodealkylation and hydrocracking reactions. Nevertheless, it appears that these undesired reactions can be minimised to enhance the methylation reaction, by using zeolites with reduced Brønsted acidity or containing alkali metal cations.

3 Utilisation of methane in coal liquefaction (or hydrogenation)

3.1 Coal and the mechanism of coal hydrogenation process

Coal is combustible rock consisting mainly of an organic material mixed with some inorganic compounds. It is a hydrogen deficient energy source and its chemical structure can generally not be defined as it is an heterogeneous combination of variable components. The mechanism of the coal hydrogenation process is therefore complex and depends on the type of coal and the severity of reaction conditions such as temperature and hydrogen pressure. Hence, reactions are only understood in general terms. Coals are classified into different ranks according to the degree of coalification, *i.e.* the degree of the chemical change that has taken place due to the decay of the original organic matter from which the coal was formed. Lignite, sub-bituminous, bituminous and anthracite are different ranks of coal. Anthracite, which has the lowest H/C ratio, is the highest ranked coal, while lignite, having highest H/C ratio, is the least coalified.

The development of coal as a source of chemical feedstocks or liquid fuel has experienced a long history. It has been responsible for powering the industrial revolution in Europe and America for more than a century. However, since World War II, coal as a primary energy source has been somewhat controlled by access to crude oil, which is cleaner and more convenient to handle and process. However, coal may once again become a major source of liquid fuels and organic chemicals if coal gasification and direct liquefaction *via* hydrogenation become economically feasible. Low ranked coals, such as lignite and bituminous coals, may be used as a source

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of a liquid fuel (synthetic crude) by raising their H/C ratio to a level comparable to that of some crude oils. This could be done by a non-catalytic or a catalytic hydrogenation process.

Coal liquefaction is normally carried out in the pressure range of 200–250 bar and temperature range of 400–450 °C. Lower pressures and short contact times produce heavier liquids while higher temperatures and long contact times reduce liquid yield and increase the amount of gases produced.[41] Iron oxide, iron oxide mixed with alumina, molybdenum and cobalt oxides supported on a highly porous alumina, and oxides of other metals such as nickel and tungsten or their mixtures are used as catalysts for the liquefaction of coal.[41] These catalysts are similar to those used in the hydrodesulfurisation reaction which, together with hydro-denitrogenation reaction, takes place during the hydro-liquefaction of coals.[41]

It is generally believed that coal liquefaction occurs *via* a free radical mechanism, and one of the earlier mechanistic details was provided by Curran *et al.*[42,43] The mechanism involves a free radical process in which coal is thermally decomposed into free radicals, which are capped with or stabilised by abstraction of a hydrogen atom from a donor molecule, such as tetralin. Molecules smaller than the original coal are then formed from this process, thereby resulting in liquefaction. The donor molecule is then hydrogenated by molecular hydrogen such that the liquefaction process continues in a cyclic manner. This mechanism has been expanded by other workers.[44,45] Most of the hydrogen consumed in the liquefaction reaction comes from molecular hydrogen. It has also been shown that, under hydrogen pressures, the stabilisation of coal-generated free radicals by direct proton abstraction from molecular hydrogen competes favourably with the donor solvent route.[46]

3.2 Liquefaction of coal by catalytic reaction with methane

Current processes for direct coal liquefaction utilise expensive hydrogen (H_2) gas at high pressures. The total hydrogen consumption is usually about 3–5% by weight of the coal feed and most of this hydrogen comes from molecular H_2, while the donor solvent acts mainly as shuttle medium for the H_2 supply[47] to enhance the hydrogen transfer. Previous cost analyses have shown that a substantial part of the overall operating cost of direct coal liquefaction (about 40–50%) would go into hydrogen generation.[48,49] Thus, if coal could be liquefied by using an alternative, less expensive gas, up to 50% savings would be achieved. A good substitute for hydrogen which is currently being given some consideration is natural gas, which contains mainly methane. Since methane is rich in hydrogen and has the same bond dissociation energy (ΔH°_{300K} = 439 kJ mol^{-1}) as hydrogen, the direct use of methane derived from natural gas would eliminate the expensive intermediate step of H_2 production. Homolytic scission of hydrogen is unfavourable at coal liquefaction temperatures of 400–450 °C. Hydrogen gas is activated by organic free radicals from coal and a similar activation of methane could also occur to produce methyl and methylene free radicals.

The presence of a catalyst such as Fe_2O_3 during coal liquefaction with methane would fulfil the following functions. The catalyst would first enhance the dissociation of methane into hydrogen radicals and methyl/methylene radicals. The free radicals produced would then be chemisorbed on the catalyst surface where they would be available for further reactions such as polymerisation into higher molecular weight hydrocarbons. Transition metal catalysts such as iron are known to be capable of dissociative chemisorption of C_1 molecules and hydrogen gas.[50,51] Long and co-workers have previously demonstrated that microporous aluminophospahte catalysts could activate elemental hydrogen.[52,53] The catalytic activity was enhanced by the incorporation of common metals such as lead and bismuth and these catalysts were observed to methylate toluene with methanol and to convert methanol to dimethylether. These workers have also subsequently shown that the aluminophosphate catalysts could activate methane during the methylation of naphthalene, toluene and phenol and that H-beta and Cu-beta were also capable of methylating benzene with methane.[21–23,25] A more recent investigation by Long *et al.*[26] have also demonstrated the incorporation of methane in the presence of Cu-beta, H-beta and CuZSM-5 into a variety of organic substrates which model petroleum, coal and liquefaction residue structures. The reaction was carried out at 350–400 °C and 3.5–9 MPa pressure. According to these workers, one mechanism involved direct methylation by addition of methyl groups while the other involved a disproportionation process resulting in carbon deposition.

Initially, methane was reported by Cypres and Furfari[54] to be chemically inert in their investigation of low-temperature pyrolysis of coal under pressures of H_2–CH_4 mixtures. Later, methane was reported to be very reactive in coal pyrolysis on the basis of greatly increased C_2 and liquid yields.[55,56] Since then, there now seems to be increasing evidence that methane can react directly with coal at coal liquefaction temperatures[48,49,57,58] Sundaram *et al.*[57] in a US patent have shown that in the temperature range of 350–450 °C at 6.9–17.2 MPa, more coal is converted to volatile products under methane than under argon. A hydrogen donor solvent was used in these experiments, typically with a coal-to-solvent ratio of 3 : 1. Smith *et al.*[58] have also previously reported that methane in combination with small amounts of oxygen or nitric oxide reacts with coals to produce significantly higher yields of hydrocarbons than can be obtained with either helium or methane alone. Egiebor and Gray[48] have also been able to show in 1 : 1 coal-to-tetralin ratio experiments at 450 °C and 19–24 MPa that conversions to gaseous and liquid products were higher under methane than under hydrogen. These workers further reported that during pyrolysis without tetralin, coal conversions under methane gas pressures were higher than those observed in the runs under argon atmospheres, but lower than under hydrogen. It was shown that methane was consumed in methane atmosphere experiments and that liquefaction with methane produced more than seven times as much C_2–C_5 gases as with hydrogen and eleven times the amount produced with argon. Furthermore, the hydrogen/carbon ratios of the toluene-soluble products from the methane experiments were higher than those from the argon experiments. On examining the solvent, the amounts of methylnaphthalenes formed were found to be greater under methane than under hydrogen or argon. This appears to be

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definitive proof for the reaction of methane during coal liquefaction even in the absence of catalyst. Ozawa and co-workers have provided further support for the reactivity of methane during asphalt degradation over molten tin at 400 °C.[59]

Long *et al.*[49] further demonstrated the reactivity of methane with a range of coals in the temperature range of 350–400 °C and pressure range 6.0–8.3 MPa over aluminophosphate or zeolite catalysts (CuZSM-5, zeolite beta and Cu-beta). Yields of dichloromethane extractable material were increased by using methane rather than nitrogen atmosphere and different catalysts were observed to assist dissolution to various extents. These workers observed that surface exchanged catalysts were effective but incorporation of metals during aluminophosphate lattice formation was detrimental. Aluminophosphate catalysts were also found to be unstable to water produced during coal conversion but were still able to increase extraction yields. Furthermore, these workers reported that there was a synergistic effect of methane–hydrogen atmosphere for coal liquefaction using their catalyst system, since the conversion under methane–hydrogen was close to that obtained under hydrogen alone, rather than that predicted if an inert gas had been substituted for hydrogen. It was then concluded that involvement of the methane–hydrogen mixtures rather than hydrogen alone might be beneficial in coal conversion processes. Methane incorporation may be oxidative in the presence of coal oxygen and small amounts of ketones have been observed[49] when oxygen has not been adequately removed in model compound studies. Small amounts of oxygen were also found to affect yields in model compound investigations.[49]

There may be other beneficial flow-on effects once methane is incorporated. Vassallo *et al.*[60,61] have previously demonstrated that methyl groups on coal macromolecules play a crucial role in capping radicals generated by pyrolysis and are therefore key entities in forming liquid products. Thus, methyl groups in coal or from other reagents assist in promoting oil yields from coal. Highly reactive methyl radicals actively promote liquefaction. Tetramethyl or tetraethyl lead[62] was found to be a superb additive for increasing oil yields at low hydrogen pressures.

4 Green chemistry perspectives

4.1 Advantages of the oxidative methylation reaction in light of green chemistry principles

According to the book written by Anastas and Warner,[63] green chemistry is defined as "the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products". In green chemistry, efficiency (or the concept of atom economy that focuses on optimising the incorporation of all materials used in a synthetic process into the final product) is now becoming extremely important in the design or synthesis of a chemical product. Thus, environmental, health, safety and economic considerations are now taken into account by synthetic chemists. If the tools and principles of green chemistry listed and discussed by Anastas and Warner[63] in their book are considered, the participation of methane and oxygen, and the effective use of zeolite catalysts in the aromatics methylation, as well as the thermodynamic feasibility of the reaction all contribute positively to these important considerations and focus of green chemistry. In the light of these tools and principles of green chemistry, the advantages of the oxidative methylation reaction and areas for further development are clearly identified and discussed as follows:

The use of methane in the methylation reaction to produce the value-added higher aromatics is definitely advantageous as it is a very destructive greenhouse gas. Methane conversion is also important because the gas is a hydrogen-rich reagent; thus, this methylation route could be applied in production of liquid hydrocarbons by direct coal liquefaction with methane rather than with the more expensive and hazardous hydrogen that is commonly used in current processes.

The effective catalytic conversion of methane is beneficial, as the use of catalytic reagents is generally superior to stoichiometric reagents. In particular, the fact that zeolite catalysts are active for the oxidative methylation reaction has positive green chemistry implications as they are relatively non-hazardous. Of course, better catalysts can still be developed and the knowledge gained from previous studies by Adebajo and co-workers[27,28,38] that moderate acidity is all that is needed for the activity of the catalysts can be taken into consideration in the development of more active and selective catalysts.

Although, an intermediate oxidation step requiring stoichiometric use of oxygen is involved in the reaction, air or at worst safe amounts of oxygen below the explosive limit of oxygen/methane mixtures can be used as the auxiliary substance for the oxidation step.

The high thermodynamic feasibility and exothermic nature of this oxidative methylation reaction are crucial as it is thus possible to conduct the reaction, using air or oxygen, more safely at much lower pressures (or even atmospheric pressure) and temperatures. It is no longer necessary to carry out the reaction under high methane pressures to drive the reaction forward towards the production of methylated products. Consequently, the reaction has higher energy efficiency, especially as the route is also catalytic. The conduction of the reaction at atmospheric or close to atmospheric pressures and lower temperatures than previously investigated, especially using a flow reaction system, is an area that is identified for further study.

Finally, it is worthwhile to note that only water is produced during the oxidative reaction in addition to the industrially important higher aromatics; no CO, CO_2, or H_2 were detected in gas products of the reaction as reported by Adebajo *et al.*[32] Thus, there appears to be no significant complete or incomplete combustion of methane during the reaction.

4.2 Evaluation of the "greenness" and efficiency of the oxidative methylation reaction using green chemistry metrics

The quantitative determination of the greenness of the oxidative methylation reaction described in this article is important for the identification of any hazardous or inefficient procedures with unfavourable environmental impact as well as for minimization of cost. Such quantitative evaluation would

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Table 7 Reaction metrics for oxidative benzene methylation with methane (eqn (15)) and the more traditional benzene methylation with methanol (eqn (14))

	Oxidative benzene methylation with methane using HZSM-5 catalyst (eqn (15))		Benzene methylation with methanol reaction (eqn (14))		
	Experiment 1 using 0.31% O_2	Experiment 2 using 2.1% O_2	HZSM-5 catalyst	CoZSM-5 catalyst	CuZSM-5 catalyst
Benzene conversion (%)	4.17	10.1	44.3	46.4	46.5
Methanol conversion (%)	—	—	74.6	76.0	75.9
Toluene selectivity (%)	93.0	84.6	52.2	52.0	53.5
Toluene yield (%)	3.88	8.54	23.1	24.1	24.9
Atom economy (%)	83.6	83.6	83.6	83.6	83.6
Carbon efficiency (%)	93.0	84.6	107.3	102.7	105.5
Reaction mass efficiency (%)	77.8	70.8	82.2	79.1	81.3
Effective mass yield (%)	91.1	82.8	82.2	79.1	81.3
Mass intensity/kg kg^{-1}	4.23	2.75	3.18	3.24	3.15
Mass productivity (%)	23.6	36.4	31.4	30.9	31.8
Raw material cost/\$ kg^{-1}	2934.34	1331.80	136.33	130.66	126.72
Raw material cost at 100% yield/\$ kg^{-1}	113.80	113.80	31.53	31.53	31.53

therefore enable one to identify areas for improvement, thus optimizing the process accordingly. Various green chemistry metrics that allow for measured, objective analysis for comparison of competing reactions and processes have been developed and recently reviewed.[64] It is always necessary to consider the purposes of evaluation prior to the choice of metrics. For example, in the evaluation of an industrial process, metrics that emphasize the measurement of efficiency and cost, in addition to evaluation of chemical hazards would prove to be most useful. It is generally agreed that good and useful metrics must be clearly defined, simple, measurable, objective, and must ultimately drive the desired behaviour.[65] According to the review by Constable *et al.*,[64] some of the metrics that have been developed include Trost's atom economy[66] (AE), effective mass yield[67] (EMY), E-factor[68,69] (EF), mass intensity[64,70] (MI), mass productivity[64] (MP), carbon efficiency[70] (CE) and reaction mass efficiency[70] (RME). Andraos[71] has also recently assessed another metric known as the raw material cost (RMC) for evaluating the costs of raw materials that are used in the particular chemical reaction or process. Energy intensity (EI) metrics has also been used to quantitatively evaluate energy usage.[65,72,73]

As shown in Tables 7 and 8, all these metrics, except the E-factor, have been used to quantitatively determine the greenness of the oxidative benzene methylation with methane. The more traditional or commercial alkylating agents for the alkylation of aromatics are alkyl halides, alcohols and ethers, alkenes, alkynes and dienes.[74–77] Incidentally, the second step of the oxidative benzene methylation with methane is the more traditional benzene methylation with methanol. As mentioned earlier in section 2.1, the results of the investigation of benzene methylation with methanol over zeolite catalysts have demonstrated excellent correlation of the performance of catalysts for both this traditional methylation reaction and the new oxidative methylation with methane.[37] The metrics for the oxidative methylation reaction are therefore also compared with the values for the more traditional methylation of benzene with methanol (Tables 7 and 8). EF is a measure of the amount of waste produced per unit mass of desired product, and it takes into account the mass of the materials used in the process including water that is a benign waste. The generation of significant amounts of such a benign waste like water can make the environmental impact appear to be much worse than it actually is. Thus, instead of EF, the effective mass yield, EMY is used in this study. This is because EMY, which is expressed as the percentage of the mass of desired product relative to the mass of all non-benign materials used in the reaction or process, excludes any benign materials such as water, dilute ethanol or acetic acid or low concentration of benign inorganic salts. EMY is actually approximately the reciprocal of EF expressed as a percentage.

The values of percentage of benzene and methanol conversion, toluene selectivity and toluene yield for both types of methylation reaction are included in Table 7. Data and sample calculations used to calculate all the metrics in Tables 7 and 8 are presented in the ESI†. Table 7 shows that the yield of

Table 8 Energy Intensity metrics at 298 and 673 K for the same reactions (eqn (15) and (14) as in Table 7

	Oxidative benzene methylation with methane (eqn (15))	Benzene methylation with methanol reaction (eqn (14))
ΔG at 298 K/kJ mol^{-1}	−185.8	−74.0
K_{eq} at 298 K	3.7×10^{32} $(L\ mol^{-1})^{1/2}$	7.76×10^{12}
ΔG Energy intensity at 298 K/MJ kg^{-1}	−2.02	−0.80
ΔH at 298 K/kJ mol^{-1}	−200.1	−73.7
ΔH Energy Intensity at 298 K/MJ kg^{-1}	−2.17	−0.80
ΔG at 673 K/kJ mol^{-1}	−168.2	−75.5
K_{eq} at 673 K	7.76×10^{12} $(L\ mol^{-1})^{1/2}$	7.18×10^{5}
ΔG Energy intensity at 673 K/MJ kg^{-1}	−1.83	−0.82
ΔH at 673 K/kJ mol^{-1}	−198.3	−71.0
ΔH Energy intensity at 673 K/MJ kg^{-1}	−2.15	−0.77

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toluene in the oxidative methylation reaction is much lower than that of the methylation with methanol reaction. However, the selectivity to toluene is actually much higher in the oxidative methylation reaction and it has been demonstrated that the oxidative methylation reaction is limited by the amount of oxygen in the reactor.[32] Thus, both benzene conversion and toluene yield increased with increase in amount of oxygen in the reactor. So, it is possible to raise the yield of toluene in the oxidative methylation reaction to compare favourably with that of benzene methylation with methanol by increasing further the amount of oxygen in the reactor. However, one should ensure that the amount of oxygen does not exceed the explosive limit of the oxygen–methane mixture.

Atom economy is a measure of how much of the reactants remain in the final product. Reaction yield and molar excesses of reactants are ignored in the calculation of this metric. Solvents and reagents are also not taken into consideration in the calculation of AE. It has been suggested that AE alone would not be enough to indicate whether a process for synthesizing a material is 'greener' or 'cleaner'.[70] Nevertheless, Table 7 shows that AE is same value of 83.6% for both types of methylation reactions which is quite good. It is less than 100% due to formation of water as a by-product. The product yield and stoichiometry of reactants and products are accounted for in the calculation of carbon efficiency. CE is the percentage of carbons in the reactants that remain in the final product. The CE values listed in Table 7 for the oxidative methylation reaction account for the less than 100% yield of toluene produced. On the other hand, the CE of more than 100% obtained for methylation with methanol reactions reflects the much higher methanol conversion than benzene conversion. This high methanol conversion has been demonstrated to be due to methanol conversion over the acidic zeolites into aromatic products and secondary alkylation reaction of methanol with benzene that involves consumption of additional methanol molecules.[31]

Reaction mass efficiency is the percentage of the mass of the reactants that remain in the desired product. Atom economy, yield and the stoichiometry of reactants are included in the calculation of RME. This metric is regarded to be probably the most helpful metric for chemists to focus attention on how far from 'green' current processes are being operated.[64] According to Constable *et al.*,[64] RME is more likely to drive chemical and technology innovations that will lead to more sustainable business practices. It is therefore very encouraging that RME values obtained for the oxidative methylation reaction are again quite good and compare favourably with those obtained for methylation with methanol reactions, as shown in Table 7.

The concept of effective mass yield was proposed by Hudlicky *et al.*[67] and is calculated as the percentage of the mass of desired product relative to the mass of all non-benign materials used in its synthesis. This metric therefore gives a good indication of greenness of reactions and processes. In the oxidative methylation reaction considered in this paper, non-benign reagents were taken to be those that are classified as hazardous in the MSDS according to the criteria of National Occupational Health and Safety Commission (NOHSC) of Australia, namely benzene and oxygen. For the methylation with methanol reaction, methanol is as well taken to be non-benign as it is also classified as a hazardous substance by NOHSC. The values of EMY listed in Table 7 indicate that the oxidative methylation reaction utilizing lower oxygen concentration is greener than the other, more traditional, methylation with methanol reaction. It is also shown that the greenness of the former reaction at the higher oxygen concentration is even still comparable to that of the later, more traditional, reaction.

The mass intensity metric was discussed extensively by Constable *et al.*[64,70] MI is defined as the total kilogram mass used in a process or process step divide by the kilogram mass of the desired product. MI takes into account the yield, stoichiometry, solvent, and the reagent used in the reaction mixture, and it is expressed on a weight/weight basis rather than as a percentage. An ideal value of MI would be close to 1. Total mass includes the masses of every substance that is used in a process or process step except the environmentally benign water, that is, reactants, solvents, reagents, catalysts, *etc*. It is clear from Table 7 that the MI values obtained for the oxidative methylation reaction are not too bad when compared to the values obtained for the more traditional methylation reaction, and that it can even be slightly better for the former reaction when higher, but safe, amounts of oxygen are used. However, future efforts need to be directed to lowering the MI values closer to 1. As suggested by Constable *et al.*,[64] the mass intensity may be more usefully expressed as mass productivity in terms of broader understanding by business managers, since the latter metric highlights utilization of resources. MP is simply the reciprocal of MI expressed as a percentage. In other words, MP is the percentage of the desired product in the total mass used in a process or process step. The MP data in Table 7 indicates that only a slightly higher amount of the total mass used in producing the desired toluene product is wasted in the oxidative methylation reaction (76.4%) than in the methylation with methanol reaction (68–69%). The MP value of 36.4% in the oxidative methylation reaction utilizing a higher, but safe, amount of oxygen also indicates that it is possible to achieve wasting even smaller amounts of the total mass used in the toluene production by increasing the amount of oxygen.

The concept of raw material cost was recently discussed by Andraos.[71] In calculating RMC, the costs per unit mass of the reagents, the stoichiometry and the product yield are accounted for. The RMC at 100% yield, denoted by RMC_{100} can be obtained by multiplying RMC by the product yield. RMC data in Table 7 were obtained by using the costs of the largest quantities in the catalogues of Sigma–Aldrich and BOC for high purity grades of the liquid and gaseous reactants, respectively. The costs of the catalysts are, however, not included in the calculations. The data for calculating the RMC values in Table 7 and sample calculations are included in the ESI.† The RMC data in Table 7 shows that the oxidative methylation reaction is much more expensive than the benzene methylation with methanol reaction. However, the data also shows that the cost of the former reaction can be brought closer to the later reaction again by using a higher (but safe) amount of oxygen, thus increasing the yield of the toluene product and wasting much less of the total mass used in toluene production, as discussed earlier. The lowering of the cost by increasing the product yield is reflected in the RMC_{100} value for the oxidative reaction, which is now even much closer

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to that obtained for the methylation with methanol reaction. Both RMC and RMC_{100} can also be lowered by using less expensive air instead of oxygen as the auxiliary substance for the oxidation step. Another factor that must have contributed to the much higher RMC values for the oxidative methylation reaction is the use of the very expensive BOC methane gas used in the oxidative methylation reaction. As pointed out by one of the referees, improved utilization of methane could lead to significant future industrial importance, especially as methane produced by animal and vegetable metabolic processes is a renewable resource that is not well recognized. The use of methane, and even benzene, obtained from such renewable biological feedstock could also significantly lower the cost of the oxidative methylation reaction.

Lastly, the values of the thermodynamic parameters, ΔG and ΔH were used to estimate the energy intensity values at 25 and 400 °C for both types of methylation reaction and the data obtained are presented in Table 8. The EI values are expressed as MJ kg^{-1} toluene product. The equilibrium constants for both reactions at the two temperatures are also included in Table 8 for comparison. The data in Table 8 clearly indicates that the oxidative methylation reaction is more energy efficient and more feasible than the traditional use of methanol as methylating agent. In particular, it is also shown in Table 8 that the oxidative methylation reaction appears to be more spontaneous and slightly more energy efficient at the lower temperature. The conduction of the oxidative methylation at lower temperatures and pressures than previously investigated using a flow reaction system has earlier been identified as an area for further investigation. The conduction of the reaction at such milder reaction conditions can also ultimately lower the cost of the reaction.

It is therefore clear from the foregoing discussion that the greenness of the oxidative methylation reaction is quite good and compares favourably with the more traditional methylation with methanol reaction. Interestingly, the methylation with methanol is also actually the second step of the oxidative methylation route. In other words, the production of methanol (*via* the partial oxidation of methane) for methylating the aromatic hydrocarbon is incorporated into the oxidative methylation route, and therefore constitutes a big advantage.

5 Conclusions

This paper provides a general overview of the recent work that has been done on the use of methane for catalytic methylation of aromatic compounds and for direct liquefaction of coal for the production of liquid hydrocarbons. Such methylation reactions constitute a new route for the utilisation of methane derived from natural gas or other sources for conversion to more valuable hydrocarbons. In conclusion, it is shown clearly from the review that the activation of methane for subsequent reaction with aromatics and coal is made easier in the presence of oxygen to yield methylated products The oxidative methylation mechanism therefore appears to be a common feature of methylation reactions with methane. Zeolites which have been commonly used as catalysts provide the required acid sites of moderate strength. Strong acidity, such as that exhibited by H-beta, causes cracking of aromatics and should be avoided. Traces of ethylene impurities in the methane used have significant effect on benzene conversion and product selectivity. These results have now resolved the lack of agreement in previous reported studies with respect to methane incorporation into the methylated products. Positive green chemistry implications of these findings include the following:

(1) Catalytic conversion of greenhouse methane *via* this route to value-added chemicals which are important to petrochemical industry.

(2) As methane is a hydrogen-rich reagent, this oxidative methylation route could be applied in production of liquid hydrocarbons by direct coal liquefaction with methane rather than with the more expensive and hazardous hydrogen that is commonly used in current processes

(3) Only water is produced during the oxidative reaction in addition to these industrially important higher aromatics. No CO, CO_2 or H_2 was detected in gas products.

(4) Relatively non-hazardous zeolite catalysts are active for the reaction.

(5) Air, or at worst safe amounts of O_2 below the explosive limit of oxygen–methane mixtures, can be used as the auxiliary substance for the oxidation step.

(6) Due to the high thermodynamic feasibility and exothermic nature of the oxidative reaction, it is possible to conduct the reaction, using air or O_2, more safely at atmospheric pressure and much lower temperatures with higher energy efficiency than previously investigated. This is an area that is identified for further study.

(7) The greenness, cost-effectiveness, material and energy-efficiency are quantitatively substantiated using a variety of reaction metrics and are demonstrated to compare favourably with the more traditional or commercial use of methanol as the methylating agent.

(8) An advantage of the oxidative methylation route is the incorporation of the methanol production by the partial oxidation of methane for subsequent use in methylating the aromatic hydrocarbon as it is done in the more traditional methylation method.

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