The methylation of benzene with methane over zeolite catalysts: effect of hydrocarbon impurities

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Received 24 August 2000; accepted 2 January 2001

Trace amounts of ethylene impurities in the methane used for benzene methylation over ZSM-5 and H-beta catalysts are found to enhance benzene conversions and selectivity to ethylbenzene. However, methane containing ethane impurities yielded negligible benzene conversion in the absence of oxygen over CoZSM-5 while a much higher conversion is obtained over H-beta due to cracking of benzene as previously reported.

KEY WORDS: methane activation; benzene methylation; ZSM-5; H-beta; hydrocarbon impurities

1. Introduction

Considerable interest is presently shown in the conversion of methane, the major component of natural gas, to transportable liquid fuels and feedstocks in addition to its previous main use for heating purposes by combustion. The methylation of aromatic compounds with methane is one possible new route for methane conversion that has been described recently in the literature. For example, the methylation of naphthalene, toluene and phenol with methane over various metal substituted aluminophosphate molecular sieves in a high pressure batch reactor has been reported [1,2]. The conversion of benzene in the presence of methane over zeolite catalysts in both high pressure flow reactor [3] and batch reactor [4] has also been described. However, the high pressure flow reactor study [3] showed, through the use of ^{13}C labelled methane, that the methyl groups in the methylated aromatic products did not originate from the methane reactant.

In our more recent investigation of the methylation of benzene with methane at 400 °C over ZSM-5 catalysts in a high pressure batch reactor [5], we demonstrated clearly that the presence of oxygen was required for the reaction to proceed to yield the methylated products. Thus, a two-step mechanism involving the intermediate formation of methanol by partial oxidation of methane followed by the methylation of benzene with methanol, was postulated. Further support to this mechanism has also been reported in our later investigation [6] which showed excellent correlation between the activity of the catalysts used for both the benzene methylation with methanol and benzene methylation with methane in the presence of oxygen, in a high pressure batch reactor.

In this paper, we report the results of our preliminary investigation of the effect of hydrocarbon impurities (namely, ethane and ethylene) on the methylation of benzene with methane over ZSM-5 catalysts in a batch reactor.

2. Experimental

Commercial samples of HZSM-5 (PQ Corporation, $SiO_2/Al_2O_3 = 35$) and H-beta (PQ Corporation, $SiO_2/Al_2O_3 = 35$) were used in this study. A Co-exchanged ZSM-5 catalyst which was prepared by conventional ion exchange with aqueous cobalt nitrate was also used. All the reactions were carried out at 400 °C in a 71 ml Parr reactor fitted with a glass liner. In each experiment, 55 mg of catalyst and 465 μl of benzene were placed in the reactor which was then charged with 6.9 MPa chemically pure ($>99.0\%$ pure) or ultrahigh purity ($>99.97\%$ pure) methane. The details of the experimental procedures are similar to those published recently [5].

In order to study the effect of ethane and ethylene impurities on the benzene methylation reaction, the reactor (already loaded with the catalyst and benzene) was chilled in a chloroform slush bath and flushed several times, first with nitrogen gas to remove residual air and then with the ethane (or ethylene), prior to charging with high pressure ultrahigh purity methane. The amount of the ethane (or ethylene) introduced into the reactor was about 2.1% of the composition of the gases in the reactor excluding benzene.

The details of the GC and GC/MS analysis of reaction products and measurement of zeolite catalyst acidities using FTIR of adsorbed pyridine are similar to those described elsewhere [6].

3. Results and discussion

Table 1 summarises the results of the benzene methylation experiments over both HZSM-5 and CoZSM-5 in the

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1011-372X/01/0400-0221$19.50/0

Table 1
Effect of the purity of methane on methylation of benzene 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 2
Effect of adding ethane and ethylene to the methane used in the methylation of benzene over CoZSM-5 catalyst 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.

presence of residual air. It is shown in table 1 that the total benzene conversion was almost doubled when chemically pure (CP) grade methane was used in place of the ultrahigh purity (UHP) methane (>99.97% pure with <300 ppm sum of N_2, O_2, C_2H_4, C_{3+} and H_2O). A significant decrease in selectivity to toluene and a corresponding increase in selectivity to ethylbenzene were also obtained for the experiments involving the CP grade methane. This resulted in considerable reduction in the toluene/ethylbenzene ratio. It was therefore suspected that greater amounts of ethane or ethylene impurities in the CP grade methane might be responsible for the enhancement of benzene conversion and ethylbenzene selectivity when this type of methane was used. Thus, further experiments involving about 2.1% ethane and ethylene additives in the reaction system containing 6.9 MPa UHP methane were carried out to investigate the effects of these gases on the reaction. The results of such experiments are presented in table 2. It is shown clearly in table 2 that, over both CoZSM5 and H-beta, a much higher benzene conversion, and higher selectivity to ethylbenzene with corresponding lower selectivity to toluene were obtained for the reaction performed in the presence of 2.1% ethylene in the reaction vessel in comparison to that done in the presence of the same amount of ethane. This resulted in a much lower toluene/ethylbenzene ratio for the reaction involving the ethylene additive. Thus, the presence of ethylene additive in the methane has a much more significant effect on the benzene conversion and selectivity to ethylbenzene than the presence of ethane additive, under the reaction conditions employed in this study. Since it has been shown earlier that the presence of oxygen also has a significant effect on the benzene reaction with methane [5], the enhancement of benzene conversion and selectivity to ethylbenzene in the experiments using CP methane (table 1) can therefore be attributed to much higher levels of both ethylene and oxygen. It is shown clearly in table 1 that, in the presence of air, about 4% benzene conversion and 4% ethylbenzene selectivity are obtained in the experiments involving UHP methane containing relatively negligible amount of ethylene. This benzene conversion, in the presence of oxygen, has been shown to be the result of a two-step mechanism involving the formation of methanol intermediate by partial methane oxidation followed by methylation of benzene with methanol in the second step [5]. Hence, the additional conversion of benzene and the formation of ethylbenzene in the presence of higher levels of ethylene impurities in CP methane (table 1) is not simply the result of alkylation with ethylene alone since the reactions were conducted in the presence of residual air. However, in the experiments performed with UHP methane plus 2.1% ethylene in the absence of oxygen (table 2), it is possible that the enhanced conversion of benzene and formation of ethylbenzene may be due mainly to benzene alkylation with ethylene since no oxygen is present for the two-step oxidative methylation with methane to occur. The ethylene/benzene molar ratio of 0.64 in the feed for the table 2 experiments further indicates that ethylene, being the limiting reactant, undergoes a relatively large conversion with benzene to yield ethylbenzene.

The alkylation of benzene with ethylene over acidic zeolites is generally accepted to occur via the carbenium ion

Table 3
Reaction of ethane and ethylene with benzene in the absence of methane over H-beta at 400 °C for 4 h.

Reaction type	Total benzene conversion (%)	Selectivity (%)		Toluene/ethylbenzene ratio
		Toluene	Ethylbenz.	
No nitrogen and no methane				
C_2H_6 (1 atm) + air (1 atm)	2.54	86.0	14.0	6.14
1 atm C_2H_6 (nil O_2)	3.65	88.0	12.0	7.33
1 atm C_2H_4 (nil O_2)	33.0	29.9	58.4	0.51
N_2 used in place of CH_4 (6.9 MPa total pressure)				
Nil O_2, C_2H_6 or C_2H_4	2.40	85.2	14.8	5.76
2.1% C_2H_6 (nil O_2)	5.94	81.9	14.9	5.50
2.1% C_2H_4 (nil O_2)	35.9	24.7	60.8	0.41

mechanism [7–9]. In this mechanism, the ethylene is protonated over the Brønsted acid sites to give a carbenium ion. The carbenium ion then undergoes electrophilic attack on the aromatic π-electrons to generate a mono- or polyalkylbenzenium ion. The desorption of the latter intermediate and loss of the proton results in the gas-phase alkylated aromatic and the re-generation of the Brønsted acid sites. FTIR spectra of adsorbed pyridine for all the catalysts used showed that they all contained some Brønsted acid sites [5,10]. It is therefore possible that, in this work, ethylene promotes the conversion of benzene via this mechanism.

The higher value of 2.76% benzene conversion for the reaction system containing 2.1% ethane over the H-beta catalyst than the value of 0.60% obtained for the reaction over CoZSM-5 (table 2) may be attributed to the cracking of benzene on the catalyst occurring without participation of methane in the reaction such that benzene serves as the sole source of methyl substituents in the methylated aromatic products, as previously reported [3–5]. In order to clarify the mechanism for this different behaviour on H-beta, experiments in which ethane or ethylene was added to the reaction system in the absence of methane were carried out; some involving high pressure nitrogen replacing methane and others involving neither nitrogen nor methane in the reactor. The results of such experiments are presented in table 3. Table 3 clearly reveals again that the addition of ethylene to the reaction system has a much more significant effect on the reaction, since ethylene is much more reactive than ethane. The results presented in table 3 also further demonstrate that, in the absence of oxygen over the H-beta catalyst, methane is not directly involved in the alkylation of benzene but rather, according to Lunsford et al. [3], benzene is cracked on the catalyst into carbonaceous CH_x species which can then react with additional benzene to form toluene:

$$C_6H_6 + CH_2(s) \rightarrow C_6H_5CH_3 \tag{1}$$

In other words, in the absence of oxygen, benzene serves as the sole source of methyl groups in the substituted benzene products over H-beta. Actually, it was observed that the H-beta catalyst was always blackened during the reactions indicating some coking in the reaction systems. Previous investigation [5] has also shown that the H-beta catalyst exhibited an increase in benzene conversion with increase in the amount of oxygen. It is therefore proposed that in the presence of oxygen over H-beta, a mechanism involving a combination of indirect methylation via formation of a methanol intermediate [5] and fragmentation and rearrangement of benzene without participation of methane must be responsible for the formation of the methylated products in the reaction of methane with benzene. Thus, the conversion of benzene in the experiment involving 1 atm of ethane plus 1 atm air in the absence of both nitrogen and methane (table 3) is due mainly to cracking and coking of the benzene and some slight reaction of ethane since no methane is present to react with oxygen present in the air to form the methanol intermediate. The comparable benzene conversions and product selectivities obtained for the two experiments performed in the absence of nitrogen or methane and involving 1 atm ethane with or without air (table 3) may therefore be due mainly to the cracking of benzene over the H-beta catalyst. This mechanism involving cracking of benzene over H-beta can be attributed to its strong acidity and its larger pore size than that of ZSM-5 such that the formation of bulky reaction intermediates is more easily favoured over H-beta. This observation is consistent with a previous observation [7] that secondary alkylation and disproportionation reactions of generated alkylaromatics are favoured to a higher extent over beta zeolite than over ZSM-5 catalyst during the alkylation of benzene or toluene with methanol or ethylene.

It is worth mentioning too that table 3 indicates that pressure does not have any significant effect on the reaction since the benzene conversions and selectivities to products obtained for the low pressure experiments performed in the absence of nitrogen or methane are quite similar to the values obtained for the 6.9 MPa pressure experiments performed in the presence of high pressure nitrogen in place of methane. This observation is quite consistent with equation (1) proposed for the fragmentation and rearrangement mechanism which also indicates that the reaction is independent of pressure, the carbonaceous species, CH_x being in the solid state.

In conclusion, it is clear from this study that the purity of methane used in the methylation of benzene over zeolite catalysts is critical in determining conversion and product selectivities. The presence of trace amounts of ethylene in the methane is found to have a very significant effect on benzene conversion and selectivities to products over both CoZSM-5 and H-beta. On the other hand, the presence of ethane impurities is found to yield negligible benzene conversion over CoZSM-5 when oxygen is excluded from the reactor. However, in the absence of oxygen, a much higher level of benzene conversion is obtained with methane containing ethane impurities over H-beta due mainly to cracking of benzene.

Acknowledgement

The funding of this work by the Australian Research Council is gratefully acknowledged.

References

[1] S.J.X. He, M.A. Long, M.I. Attalla and M.A. Wilson, Energy Fuels 6 (1992) 498.

[2] M.A. Long, S.J.X. He, M.I. Attalla, M.A. Wilson and D.R. Smith, in: *Stud. Surf. Sci. Catal.*, Vol. 81, eds. H.E. Curry-Hyde and R.F. Howe (Elsevier, Amsterdam, 1994) p. 509.

[3] E.M. Kennedy, F. Lonyi, T.H. Ballinger, M.P. Rosynek and J.H. Lunsford, Energy Fuels 8 (1994) 846.

[4] S.J.X. He, M.A. Long, M.A. Wilson, M.L. Gorbaty and P.S. Maa, Energy Fuels 9 (1995) 616.

[5] M. Adebajo, M.A. Long and R.F. Howe, Res. Chem. Intermed. 26 (2000) 185.

[6] M.O. Adebajo, R.F. Howe and M.A. Long, Catal. Today 63 (2000) 471.

[7] P.G. Smirniotis and E. Ruckenstein, Ind. Eng. Chem. Res. 34 (1995) 1517.

[8] P.B. Venuto, Micropor. Mater. 2 (1994) 297.

[9] C.T. O’Connor, E. Van Steen and M.E. Dry, in: *Stud. Surf. Sci. Catal.*, Vol. 102, eds. H. Chon, S.I. Woo and S.-E. Park (Elsevier, Amsterdam, 1996) p. 323.

[10] M.O. Adebajo, Ph.D. thesis, University of New South Wales, Australia (1999).