

The Contribution of the Methanol-to-Aromatics Reaction to Benzene Methylation over ZSM-5 Catalysts

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Abstract

The methanol to aromatics conversion is shown to contribute significantly to the benzene methylation with methanol at 400 °C over acidic ZSM-5 catalysts but such contribution over all catalysts is negligible at 250 °C. Benzene-only conversion shows only negligible contribution at both temperatures over the catalysts studied. However, it appears that the methanol-only conversion can be minimised, to enhance the benzene methylation with methanol (and indirectly the oxidative benzene methylation with methane), by using NaZSM-5 with highly reduced Brønsted acidity.

Keywords: Benzene methylation, methanol, methane, methanol-only conversion, benzene-only conversion, methane conversion, ZSM-5.

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1. Introduction

Our recent investigations [1,2] have shown clearly that the presence of oxygen was required to yield the methylated products in the methylation of benzene with methane at 400 °C over ZSM-5 catalysts in a high pressure batch reactor. It was also observed 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 % methanol selectivity [2]). Furthermore, the methanol was not detected in the presence of the zeolite catalysts when oxygen was introduced into the reactor indicating that all the methanol, being more reactive than the initial methane reactant, was consumed to form methylated products over the catalysts. Thus, the reaction was postulated to go via a two-step mechanism involving the intermediate formation of methanol by partial oxidation of methane followed by the methylation of benzene with methanol in the second step. Further support to this mechanism has also been reported in our later investigation [3] which showed excellent correlation between the activity of the catalysts used for both the benzene methylation with methanol in a low pressure flow reactor and benzene methylation with methane in the presence of oxygen in a high pressure batch reactor.

An important observation of the conversion data presented in our later investigation [3] is the consistently higher values of methanol conversions in all the reactions involving equimolar amounts of methanol and benzene reactants. Smirniotis and Ruckenstein [4], in their study of the alkylation of benzene with methanol over ZSM-5 catalyst, have also previously reported higher methanol conversions than benzene conversions. The Brønsted acid catalysed conversion of methanol to predominantly isoparaffins and C₆ - C₁₀ aromatic compounds over acidic ZSM-5 zeolites as previously observed at 370 °C and 1 atmosphere pressure [5] might actually have contributed greatly to the higher methanol conversions. It is also possible that secondary alkylation and oligomerisation reactions involving consumption of additional methanol molecules might contribute to the higher methanol conversions. This paper therefore reports the results of our experiments involving only pure methanol and pure benzene over HZSM-5, NaZSM-5

and CuZSM-5 at 250 °C and 400 °C in a low pressure flow reactor in order to determine the contributions made by methanol conversion to benzene and higher aromatics and by benzene conversion to the methylation of benzene with methanol. It should be noted that these catalysts are three of the same catalysts used in our earlier investigation of the methylation of benzene with methanol. Since excellent correlation has been shown to exist between the activity of the catalysts used for both the benzene methylation with methanol and the oxidative methylation of benzene with methane involving methanol intermediate formation, the knowledge of such contributions is quite relevant to the development of better catalysts for the later reaction.

2. Experimental

The catalyst used in the study was a commercial sample of HZSM-5 (PQ Corporation, SiO₂/Al₂O₃ = 35). The Na-exchanged catalyst (NaZSM-5) which was also used was prepared by conventional ion exchange into the HZSM-5 sample with aqueous sodium nitrate solution. The ion exchange was done three times. The NaZSM-5 obtained by performing ion exchange once with aqueous sodium nitrate was then used to prepare Cu-exchanged zeolite (CuZSM-5) by conventional ion exchange with aqueous copper nitrate solution. The ion exchanged catalysts were then washed several times with deionised water and oven dried overnight at 100 °C.

Catalytic experiments were conducted at 250 °C and 400 °C and 1 atmosphere pressure in a fixed-bed continuous flow reaction system using a thick-walled stainless steel reactor with a fused-glass liner. The reactor was about 380 mm long, 6.35 mm outside diameter and 3 mm actual inside diameter. In each run, 200 mg of catalyst was pelletised, crushed and sieved to 24 - 42 mesh (355 - 710 µm) before loading into the reactor. Pure methanol or benzene was then introduced directly into the reactor at the rate of 0.3 mL/hr (i.e. WHSV = 1.3 hr⁻¹) by a Sage Instruments syringe pump (Model 341A). High purity (99.99 %) nitrogen flowing at a rate of about 20 mL/min was employed as the carrier gas and Brooks Model 5850-TR mass-flow controller equipped with a four-channel Brooks

control and electrical read-out equipment (Model 5878) was used for the regulation of the nitrogen flow.

The details of the GC and GC/MS analyses are similar to those described in our recent paper [3]. The description of the characterisation of zeolite acidities using FTIR spectra of adsorbed pyridine have also been reported elsewhere [3].

For the methanol-only reactions, equations 1-3 for calculating the methanol conversion and product selectivities and yields were derived by taking into consideration the FID molar response factor of methanol relative to benzene (methanol/benzene molar response ratio as determined in this work = 1:9.1 or 0.11:1), the number of moles of methanol required to form 1 mole of each of the aromatic products and the differences in the FID responses of the aromatics due to differences in the number of carbon atoms:

$$\text{Methanol conversion} = \frac{6\sum C_n}{6\sum C_n + (M/R)} \quad (1)$$

$$\text{Product selectivity} = \frac{C_n}{\sum C_n} \quad (2)$$

$$\text{Product Yield} = \frac{6C_n}{6\sum C_n + M/R} \quad (3)$$

where C_n is the peak area of each of the aromatic products, M is the peak area of the unreacted methanol peak and R (= 0.11) is the molar response factor of the methanol peak relative to benzene.

In the case of benzene-only reactions, equations 4-6 were used to calculate benzene conversion and product selectivities and yields:

$$\text{Benzene conversion} = \frac{\sum C_n / n}{(\sum C_n / n) + b / 6} \quad (4)$$

$$\text{Product selectivity} = \frac{C_n / n}{\sum C_n / n} \quad (5)$$

$$\text{Product yield} = \frac{C_n / n}{(\sum C_n / n) + b / 6} \quad (6)$$

where n is the number of carbon atoms of each of the products, b is the peak area of the unreacted benzene peak and 6 refers to the number of carbon atoms in benzene.

3. Results and Discussion

The FTIR data of the zeolite catalysts used are presented in Table 1. Table 1 shows that the CuZSM-5 and NaZSM-5 catalysts used have approximately the same amount of Brönsted acidity which is considerably lower than that of HZSM-5. The reduction in the Brönsted acid sites is reasonable as these sites are replaced by the metal ions. Our previous paper had clearly shown that the order of increasing metal exchange level obtained by ICP-AES is exactly the order of decreasing Brönsted acid concentration [6]. It therefore follows that the Cu-exchanged and Na-exchanged ZSM-5 catalysts have approximately the same level of metal exchange. It should, however, be noted that the metal ion exchange did not totally remove Brönsted acidity.

^{29}Si and ^{27}Al MAS NMR spectra showed that the zeolites used in this work contained very low levels of extraframework octahedral aluminium in addition to the normal tetrahedral framework aluminium.

Negligible products were detected by the GC at the exit stream for the reaction of pure methanol or pure benzene at 250 °C. The lack of any aromatic products at 250 °C for the pure methanol experiment is consistent with the observation that below 300 °C at low space velocity ($\text{LHSV} = 0.6\text{-}0.7 \text{ hr}^{-1}$), the main reaction of methanol is dehydration to dimethylether rather than conversion to paraffins and aromatics [7].

Representative results of the catalytic conversions of pure methanol and pure benzene at 400 °C and 55 minutes on stream are presented in Table 2. Table 2 shows that pure benzene conversions at 400 °C are very low indicating a negligible contribution from the conversion of benzene alone to the methylation of benzene with methanol and therefore to the methylation of benzene with methane in the presence of oxygen. This observation gives further support to the fact that in the reaction of benzene with methane in the absence of oxygen, the cracking of benzene does not occur over ZSM-5 catalysts to give

carbonaceous CH_x species which can then react with additional benzene to form methylated products [3,8]. Hence, the conversion of benzene was found to be very negligible (less than 0.3 %). Such cracking of benzene to give methylated products had, however, been previously observed over H-beta catalyst due to its stronger acidity and larger pore size than that of ZSM-5 [3,8,9].

Table 2 also shows that significant conversions of pure methanol were obtained at 400 °C over HZSM-5 and CuZSM-5 and aromatics (benzene, toluene, xylenes and C₉+ aromatics) were the major products detected at this temperature. The significant methanol conversions obtained over HZSM-5 and CuZSM-5 indicate that this reaction contributed greatly to the methylation of benzene with methanol over these catalysts. It should be noted that in our previous investigation [1,2] of the role of methanol in the reaction of methane with benzene in the presence of oxygen, an experiment in which HZSM-5 was used but benzene excluded also gave significant yields of aromatic hydrocarbons (mainly benzene, toluene and xylenes). Gesser et al [10] have also previously reported the conversion of pure methane to liquid hydrocarbons (with aromatics being the predominant components of the liquid hydrocarbons) via the intermediate formation of methanol over HZSM-5 catalyst in a plug-flow reactor at about 20 atm. pressure and 400 °C. On the other hand, methanol conversion over NaZSM-5 was found to be much lower indicating a much lower contribution from the methanol to aromatics conversion to the methylation of benzene with methanol. As mentioned earlier, the NaZSM-5 used for this work was obtained from HZSM-5 by performing ion exchange three times with aqueous NaNO_3 and was found to have much reduced Brønsted acid concentration. These observations are therefore not surprising since it is generally agreed that the conversion of methanol to hydrocarbons over ZSM-5 catalysts is Brønsted acid catalysed [5,11,12]. It is important to recall that this NaZSM-5 sample with highly reduced Brønsted acidity was even found to show a slightly higher or comparable methanol and benzene conversions than all the other catalysts in the methylation of benzene with methanol at 400 °C [2,3]. Furthermore, as previously reported in our earlier study [1,2], only a small amount of Brønsted acid sites is actually necessary for a catalyst to be active for the

methylation of benzene with methane in the presence of oxygen since catalysts containing highly reduced Brönsted acidity were found to be reusable without loss of activity. It is therefore suggested that a metal exchanged ZSM-5 with highly reduced Brönsted acidity, such as the NaZSM-5 used in this work, is most likely going to be a much better catalyst than the other more acidic catalysts for the oxidative methylation of benzene with methane which has been previously proposed to involve the formation of methanol intermediate.

However, Table 2 also shows that CuZSM-5 which also contained highly reduced Brönsted acidity was much more active than NaZSM-5 and even slightly more active than HZSM-5 for the conversion of pure methanol to aromatic products at 400 °C. CuZSM-5 was reported in our earlier investigation [3] of the methylation of benzene with methanol to exhibit some anomalous behaviours attributed to the tendency of the Cu(II) to undergo autoreduction [13]. For example, at 250-300 °C, methanol and benzene conversions on this catalyst were found to be exceptionally low in comparison to conversions on other catalysts and significant amounts of diphenylmethane and bibenzyl were produced. The relatively high methanol conversion observed on CuZSM-5 in this work in spite of its highly reduced acidity may therefore also be attributed to this autoreduction behaviour.

It is shown too in Table 2 that the selectivities to aromatics obtained over HZSM-5 and CuZSM-5 are comparable to the values obtained by Chang et al. [7] over HZSM-5 at 371 °C. The approximately 38 % selectivity to other products besides benzene, toluene and xylenes over these catalysts actually includes about 8 to 9 % selectivity to aliphatic hydrocarbons in addition to the major C₉₊ aromatic products. The aliphatic hydrocarbons obtained could not be properly identified since the peaks detected by the GC were not properly resolved. The less active NaZSM-5 catalyst was observed to have lower selectivity to toluene (3.9 %) and xylenes (10.7 %) with corresponding higher selectivity to C₉₊ aromatics (57.2 %) and the poorly resolved aliphatic hydrocarbons (22.5 %). The higher selectivity to aliphatic hydrocarbons on NaZSM-5 is not surprising since reduced

acidity has been reported to increase the selectivity to lower olefins from which the aromatic hydrocarbons are formed through cyclisation and aromatisation [12]. Nevertheless, the total selectivity to aromatics is still much higher than the selectivity to aliphatic hydrocarbons. It should be noted also in Table 2 that the conversion of methanol to aromatics over HZSM-5 obtained in this work (33 %) is quite lower than the value of 100 % obtained by Chang et al. [7] over the same catalyst. However, no attempt is made in this work to determine whether our catalysts or set of results obtained are better than earlier literature reports but rather the focus was solely to determine the role of methanol-to-aromatics reaction and the catalyst Brønsted acidity in the methylation of benzene over the catalysts.

Over the whole period of 105 minutes on stream, the methanol conversions and product selectivities were generally observed not to show any significant variation with reaction time for the methanol-only reaction at 400 °C on all the catalysts as illustrated in Figure 1 for NaZSM-5. As reported recently for the methylation of benzene with methanol, this levelling of conversions and product selectivities may again be attributed to saturation of available Brønsted acid sites on the catalysts with increase in the conversion levels during the course of the reaction. However, Figure 1 also shows a slight decrease in methanol conversion with increase in reaction time on NaZSM-5 catalyst; from 11.6 % conversion at 5 minutes on stream to 6.4 % at 105 minutes on stream. This reduction of catalytic activity with increase in reaction time observed over NaZSM-5 may be due to further reduction in the concentration of Brønsted acid sites as the reaction proceeded. Increase in reaction time therefore appears to favour the minimisation of the contribution of methanol to aromatics reaction to the methylation of benzene with methanol (and indirectly the methylation of benzene with methane in the presence of oxygen) over the less acidic NaZSM-5.

Conclusions

In conclusion, it is clear from this work that there is significant contribution of the methanol-to-aromatics reaction to the methylation of benzene with methanol at 400 °C

over acidic ZSM-5 catalysts but such contribution is lacking or negligible at 250 °C. On the other hand, the cracking of benzene to form methylated products via the intermediate formation of CH_x species does not appear to play any significant role in the benzene methylation reaction at both temperatures over the catalysts. Thus, the methylated aromatic products obtained in the benzene methylation with methanol at 400 °C are derived mainly from the reaction of benzene with methanol to form toluene, the conversion of methanol to aromatic products and the secondary alkylation reactions of methanol with benzene whereas at 250 °C, these products are obtained mainly from benzene methylation with methanol and the secondary alkylation reactions. Nevertheless, it is also shown that it is possible to minimize the methanol-to-aromatics reaction at 400 °C in order to enhance the benzene methylation with methanol (and indirectly the oxidative benzene methylation with methane) by using zeolites with highly reduced Brönsted acidity such as the NaZSM-5 used in this work.

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Figure Captions

Figure 1. Variation of methanol conversion and selectivities to products with time for the methanol-only reaction at 400 °C over NaZSM-5 (WHSV = 1.3 hr⁻¹; NaZSM-5 obtained from HZSM-5 by ion exchange three times)

Table 1. Characterisation of acidity of ZSM-5 Catalysts by FTIR Analysis

Catalysts	Acid sites from FTIR of adsorbed pyridine	
	Brönsted sites	Lewis sites
	(μc) ⁻¹	(μc) ⁻¹
HZSM-5	4.2	1.0
NaZSM-5	0.7	2.8
CuZSM-5	0.6	1.5

*The NaZSM-5 sample used was prepared by performing ion exchange on HZSM-5 three times with aqueous NaNO₃.

Table 2: Conversion data and aromatics product distribution in the conversion of pure methanol and pure benzene^a

	HZSM-5 ^b	NaZSM-5	CuZSM-5	Lit. values ^c
<u>Pure methanol run</u>				
Methanol conversion, mol %	32.8 (33.0)	8.9	43.9	100
Selectivity, mol % :				
Benzene	6.9 (7.4)	5.7	3.5	4.1
Toluene	24.7 (27.2)	3.9	26.4	25.6
Xylenes	30.4 (32.0)	10.7	32.2	41.8
Others (mainly C9+ aromatics)	38.0 (33.4)	79.7	37.9	26.5 ^d
Yield, mol %:				
Benzene	2.3 (2.4)	0.51	1.5	-
Toluene	8.1 (9.0)	0.35	11.6	-
Xylenes	10.0 (10.5)	0.95	14.1	-
Others (mainly C9+ aromatics)	12.4 (11.0)	7.1	16.7	-
<u>Pure benzene run</u>				
Benzene conversion, mol %	0.64	-	0.13	-
Selectivity, mol %:				
Toluene	24.0	-	12.6	-
Xylenes	12.1	-	0.0	-
Others (mainly C9+ aromatics)	63.9	-	87.4	-
Yield, mol %:				
Toluene	0.15	-	0.02	-
Xylenes	0.08	-	0.0	-
Others (mainly C9+ aromatics)	0.41	-	0.11	-

^a Reaction conditions: WHSV = 1.3 hr⁻¹ for pure methanol or pure benzene; 55 minutes on stream; 400 °C

^b Duplicate run values for HZSM-5 are written in brackets.

^c The literature values are the values obtained for aromatics distribution over HZSM-5 at 371 °C, LHSV = 1 hr⁻¹ and 1 atm. as reported by Chang and Silvestri in reference 7.

^d This literature value is for C9+ aromatics products only.

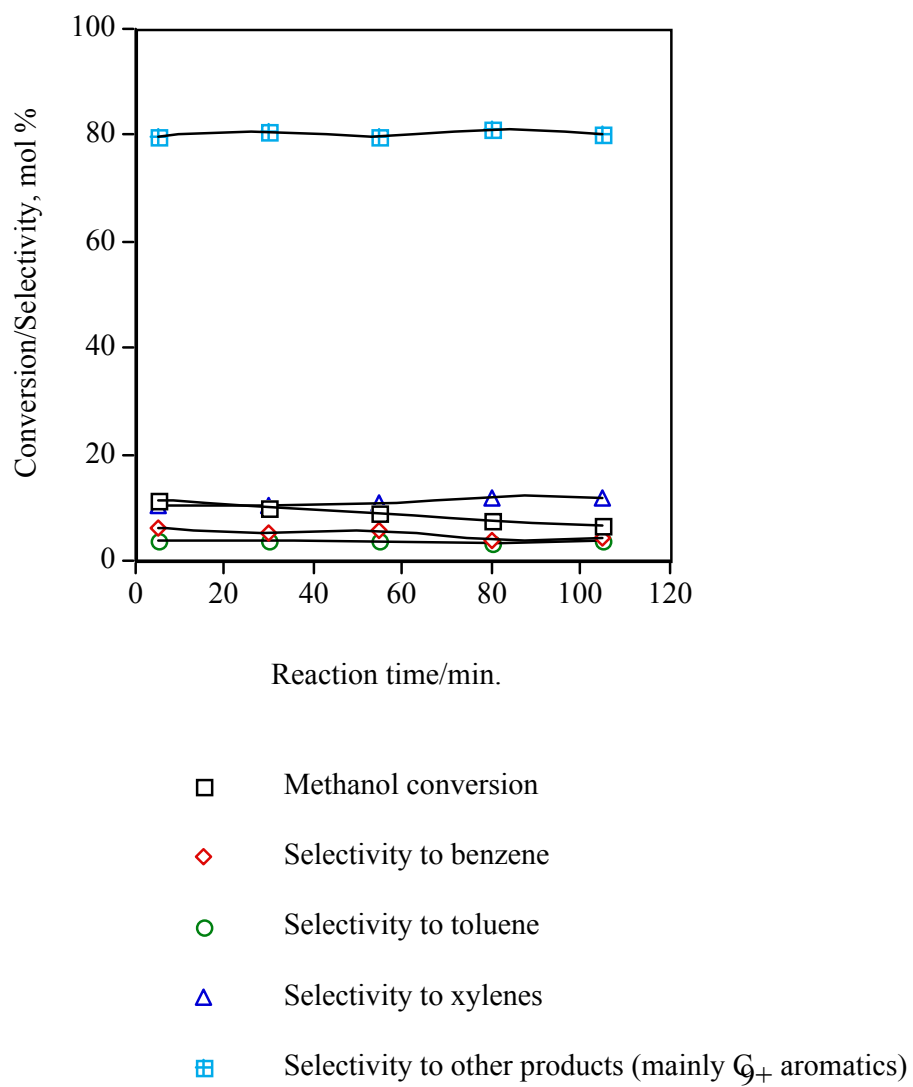


Figure 1