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Methylation of benzene with methanol over zeolite catalysts in a low pressure flow reactor

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Abstract

Previous studies in this laboratory have shown oxygen to be a crucial requirement for the reaction of methane with benzene over zeolite catalysts at 400°C in a high pressure batch reactor. Thus, 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, was postulated. This paper now shows clearly that there is excellent correlation between the performance of the zeolite catalysts used for the methylation of benzene with methanol in a low pressure flow reactor and the methylation of benzene with methane in the presence of oxygen in a high pressure batch reactor. This finding therefore gives further support to the two-step mechanism for the oxidative methylation reaction at 400°C. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Methylation; Benzene; Methanol; Methane; Zeolites' performance; Excellent correlation

1. Introduction

It has previously been demonstrated by Long and co-workers [1] that the direct methylation of benzene with methane occurred over zeolite catalysts at 400°C in a high pressure batch reactor. The methyl groups incorporated into the methylated products were shown through the use of ^{13}C labelled methane to originate from the methane reactant. Such direct methylation of aromatic molecules with methane 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 sufficient excess of methane.

In contrast to the observation by Long et al., earlier studies by Lunsford et al. [2] failed to show the presence of any detectable ^{13}C in the toluene and xylenes formed when benzene was reacted with methane at 400°C over acidic H-beta zeolite catalyst in a high pressure flow reactor. These workers concluded that the methylated products were formed by cracking of the benzene reactant, and found that the activity for this reaction was only present in strongly acidic zeolites.

A more recent investigation in this laboratory [3,4] has now demonstrated that oxygen is required in the methylation of benzene with methane at 400°C over ZSM-5 zeolite catalysts in a high pressure batch reactor. The reaction was therefore postulated to go through a two-step mechanism involving the intermediate formation of methanol by partial oxidation of methane in the first step and methylation of benzene with methanol in the second step. In addition to this oxidative methylation reaction, it was observed that in the case of H-beta zeolite catalyst, methyl aromatics can also be formed in the absence of oxygen, consistent with the earlier report [2] that these products are

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formed from cracking of benzene over the acidic zeolite.

In this paper, we report the results of the testing of the same zeolite catalysts used for the methylation of benzene with methane in the presence of oxygen for their activity for the methylation of benzene with methanol in a low pressure flow reaction system. It is observed in this work, that there is excellent correlation between the performance of the zeolite catalysts used for the methylation of benzene with methanol and the high pressure oxidative methylation of benzene with methane. This finding therefore provides more evidence for the two-step mechanism for the oxidative methylation reaction at 400°C over zeolite catalysts.

2. Experimental

The catalysts used in this study were commercial samples of HZSM-5 (PQ Corporation, $SiO_2/Al_2O_3 = 35$), H-beta (PQ Corporation, $SiO_2/Al_2O_3 = 28$) and Na-Mordenite (Toyo Soda Manufacturing Company, $SiO_2/Al_2O_3 = 20.4$, $Na_2O = 5.1$ dry weight %). The HZSM-5 was also converted to Co, Cu, and Na forms by conventional ion exchange with aqueous metal salts. The ion exchanged catalysts were then washed several times with deionised water and oven dried overnight at 100°C.

All catalytic experiments were carried out over a temperature range of 250–450°C at atmospheric 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 catalytic experiment, 200 mg of catalyst was pelletised, crushed and sieved to 24–42 mesh (710–355 μm) prior to loading into the reactor. Pre-mixed solutions of methanol and benzene, in desired molar ratios were introduced directly into the reactor at the rate of $0.3\,ml\,h^{-1}$ (i.e. WHSV = $1.3\,h^{-1}$ for the methanol plus benzene mixtures) by a Sage Instruments syringe pump (Model 341A). The methanol/benzene molar ratios were varied from 0.5 to 2.0. High purity (99.99%) nitrogen flowing at a rate of about $20\,ml\,min^{-1}$ 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.

On-line gas analyses of the reaction products were done using a Hewlett-Packard (HP 5890A) gas chromatograph equipped with a 50% trifluoropropyl methyl polysiloxane capillary column and an FID detector. The GC temperature was temperature programmed from 40 to 160°C, it was kept at 40°C for 4 min followed by heating to 160°C at the rate of $10°C\,min^{-1}$ and finally the temperature was kept at 160°C for 4 min. GC/MS analyses of some liquid samples were performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a VG Quattro mass spectrometer for detection and identification of the reaction products. The products were separated on a DB-Wax column which was temperature programmed from 35 to 220°C at the rate of $3°C\,min^{-1}$.

Zeolite catalyst acidity measurements were carried out in an in situ flow cell system using a Bomem MB-100 FTIR spectrometer equipped with an MCT detector. The cell is similar to that used by Katzer et al. [5] and to that later used by Campbell et al. [6]. Zeolite catalyst wafers (10–15 mg) were dehydrated by heating to 400°C in a continuous flow of nitrogen ($200\,ml\,min^{-1}$) gas for about 1–2 h followed by cooling to 100°C for recording the spectra. Subsequently, 2 μl of pyridine was introduced into the cell and allowed to react with the wafer for at least 10 min in the continuous nitrogen flow before another spectrum was recorded. The acidity of the sample was then determined by comparing the spectra obtained before and after pyridine adsorption.

3. Results and discussion

3.1. Catalyst performance

Representative results of the catalytic testing experiments are shown in Table 1 and Figs. 1 and 2 for reactions involving equimolar amounts of benzene and methanol. All the ZSM-5 and H-beta catalysts which were observed to be active for the oxidative methylation of benzene at 400°C and high methane pressure [3,4] are also clearly shown here to be active for the methylation of benzene with methanol over the temperature range of 250–450°C at 1 atm pressure.

Table 1
Conversion and selectivity data at 55 min on stream for the methylation of benzene with methanol (methanol/benzene molar ratio = 1, WHSV = 1.3 h^{-1} for methanol plus benzene mixture)

Temperature (°C)	Catalyst	Benzene conversion (mol%)	Methanol conversion (mol%)	Selectivity to products (mol%)		
				Toluene	Xylenes	Others
250	HZSM-5	26.8	48.6	47.6	23.4	29.0
	H-beta	30.9	66.2	32.4	21.1	46.5
	NaZSM-5[a]	23.5	40.4	53.7	20.3	26.0
	CoZSM-5	13.1	19.7	63.2	23.7	13.1
	NaZSM-5[b]	3.4	5.0	83.1	4.0	12.9
	CuZSM-5	1.9	4.5	32.1	2.7	65.2 (64.6)[c]
	Mordenite	0.15	0.15	100	–	
400	HZSM-5	44.3	74.6	52.2	27.0	20.8
	H-beta	48.6	74.0	59.0	29.7	11.3
	NaZSM-5[a]	47.9	84.4	47.0	29.9	23.1
	CoZSM-5	46.4	76.0	52.0	32.1	15.9
	NaZSM-5[b]	56.9	93.4	50.5	34.9	14.6
	CuZSM-5	46.5	75.9	53.5	29.5	17.0
	Mordenite	1.2	1.2	97.4	2.6	–

[a] This NaZSM-5 sample was prepared from HZSM-5 by performing ion exchange only once with aqueous $NaNO_3$.
[b] This NaZSM-5 sample was prepared by performing ion exchange on HZSM-5 three times with aqueous $NaNO_3$.
[c] The selectivity value for diphenylmethane plus bibenzyl on CuZSM-5 is written in brackets.

The Na-Mordenite zeolite, which was inactive for the oxidative methylation reaction at 400°C, is also inactive for the benzene methylation with methanol at 250–450°C.

Like in the oxidative benzene methylation experiments, toluene and xylenes are again found to be the predominant products on all the catalysts over the whole temperature range except on CuZSM-5 at 250–300°C where significant amounts of diphenylmethane and bibenzyl are obtained. As illustrated clearly in Fig. 2 (b), the more bulky C_{9+} aromatics are also found to be more easily favoured on H-beta than toluene and xylenes (especially at lower temperatures) due to its larger pore size which is consistent with the earlier observation [3] that toluene is more readily converted to these secondary reaction products over the catalyst in the high pressure batch reaction of benzene with methane in the presence of oxygen. The other products formed on all catalysts are mostly smaller amounts of trimethylbenzene and other higher aromatics.

Table 1 together with Figs. 1 and 2 demonstrate that the HZSM-5, NaSM-5, H-beta and transition metal exchanged ZSM-5 zeolites all gave comparable conversions and product selectivities to toluene and xylenes at 400–450°C similar to the behaviour of these catalysts at 400°C in the oxidative benzene methylation reaction. Table 1 also shows that at lower temperatures (250–350°C), the level of metal exchange into the HZSM-5 catalyst appears to have significant effect on the conversions and selectivities to toluene on the catalysts. It therefore follows that the Brönsted acidity of the catalysts may have some effect on the catalytic performance at lower temperatures. A detailed discussion of the effect of the concentration of Brönsted acidity on catalytic performance of the catalysts is presented in the next section. Benzene and methanol conversions on all the catalysts are generally found to increase with an increase temperature.

3.2. Effect of Brönsted acid concentration

Figs. 3 and 4 illustrate the effect of Brönsted acid concentration on the catalytic performance of the zeolite catalysts. Fig. 3a shows a linear correlation between the activity of the catalysts and the Brönsted acid concentration at 250°C. The methylation of benzene with methanol is therefore Brönsted acid catalysed. However, as a result of increasing tendency for saturation of available Brönsted acid sites, this dependence of catalytic activity on Brönsted acid concentration is not easily observed at temperatures higher

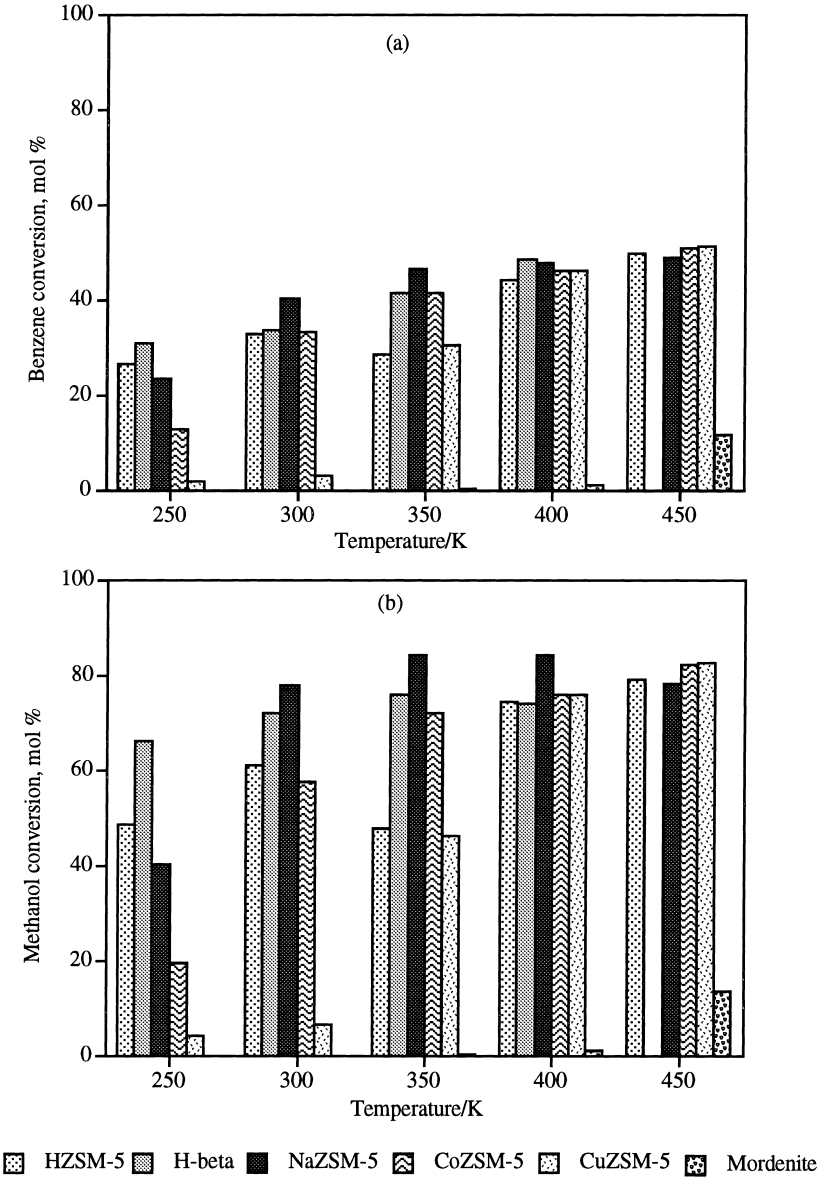

Fig. 1. The effect of temperature on (a) benzene conversion and (b) methanol conversion (methanol/benzene molar ratio = 1; WHSV = 1.3 h^{-1} for methanol + benzene; time on stream = 55 min).

than 250°C where much higher conversions are obtained. Nevertheless, the initial rise in conversions with increase in Brönsted acid concentration at 300°C (Fig. 3b) still illustrates clearly the dependence of catalytic activity on Brönsted acidity. The saturation of the acid sites is demonstrated more clearly by the levelling of conversion with increase in Brönsted acidity at 400°C (Fig. 3c).

The dependence of catalytic activity on Brönsted acidity is consistent with observation that the benzene methylation with methane in the presence of oxygen is dependent on Brönsted acid sites since methanol,

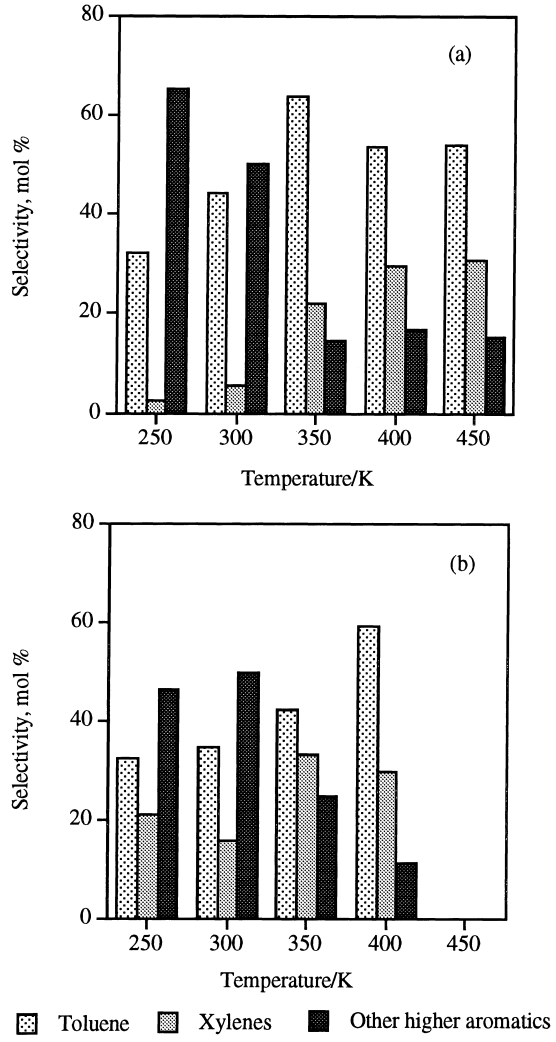

Fig. 2. The effect of temperature on selectivity to aromatic products over (a) CuZSM-5 and (b) H-beta catalysts (same reaction conditions as in Fig. 1).

which was observed to be the intermediate reaction product in that reaction, was used to methylate benzene in the second step. It should be mentioned too that the conversions at 400°C obtained on NaZSM-5 prepared by three times sodium ion exchange into HZSM-5 and CuZSM-5 (both of which are found to have highly reduced Brönsted acidity) are still comparable to those obtained at the same temperature on other ZSM-5 and H-beta catalysts (Table 1). Thus, only a small number of acid sites are actually necessary for a catalyst to be active in the benzene methylation with methanol just like the case of benzene methylation with methane in the presence of oxygen.

Fig. 4 also shows that the selectivity to toluene generally drops with increase in Brönsted acidity at 250°C which is in agreement with the observation that toluene selectivity during benzene methylation with methane in the presence of oxygen over HZSM-5 was significantly enhanced on lowering the number of acid sites of the zeolite by increasing its SiO_2/Al_2O_3 ratio from 35 to 140 [3]. However, at the very low concentration of 0.58 $(uc)^{-1}$ corresponding to that of CuZSM-5, the toluene selectivity is lowest due to formation of large amounts of diphenylmethane and bibenzyl as mentioned earlier in Section 3.1. Again, it is difficult to observe this dependence of toluene selectivity on Brönsted acidity at higher temperatures due to increased tendency for saturation of Brönsted acid sites at these temperatures where higher conversion levels are obtained. However, the comparable selectivity to toluene and other products exhibited by all the catalysts at temperatures higher than 250°C is very similar to the behaviour of these same catalysts in the oxidative benzene methylation with methane at 400°C in the high pressure batch reactor.

3.3. Effect of methanol/benzene molar ratio on catalytic activity

The effect of varying the methanol/benzene molar ratio on benzene and methanol conversions and product selectivities at 400°C over HZSM-5 and CuZSM-5 is illustrated in Fig. 5. It is shown clearly in this figure that the conversions and product selectivities on both catalysts are still comparable over the whole range of molar ratios. On both catalysts, it is observed too that the benzene conversion increases while the methanol conversion decreases with increase in the methanol/benzene molar ratio. This is reasonable since at lowest ratio of 0.5, methanol is the limiting reagent and therefore exhibits the highest conversion while benzene shows the least conversion. On the other hand, at the highest ratio of 2, benzene now becomes the limiting reagent so that the benzene now exhibits the highest conversion while methanol conversion is least.

Fig. 5 also shows that an increase in the methanol/benzene molar ratio favours the conversion of toluene

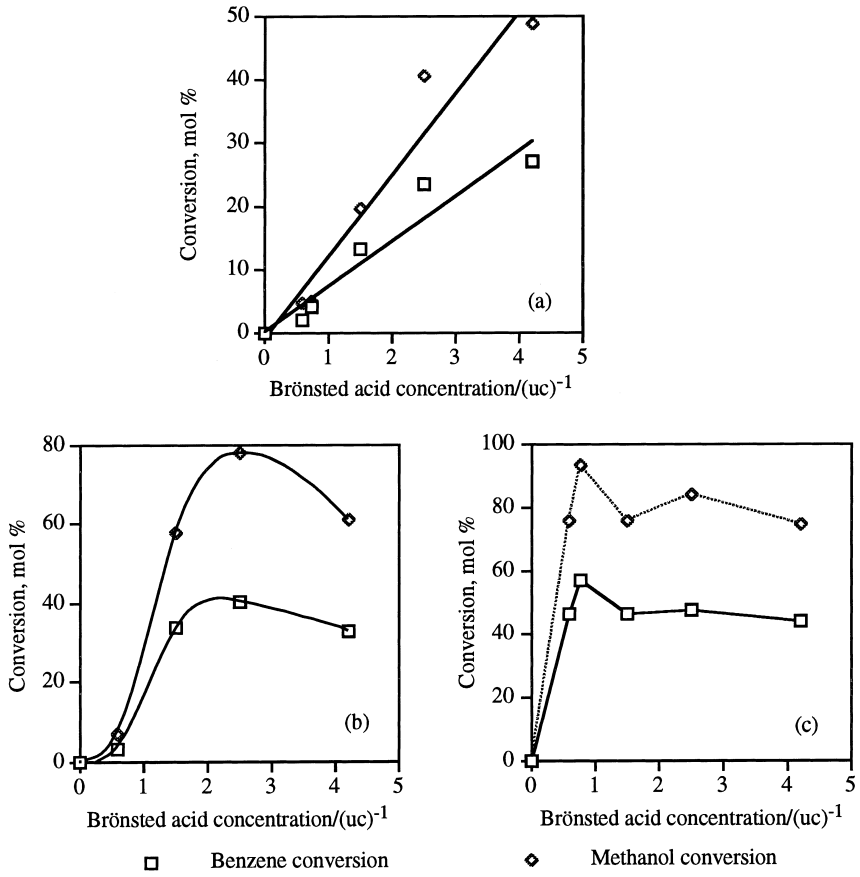

Fig. 3. Variation of benzene and methanol conversions with Brönsted acidity at (a) 250°C; (b) 300°C and (c) 400°C (same reaction conditions as in Fig. 1).

(the primary alkylation product) to xylenes and other higher aromatics (the secondary alkylation products). This is quite similar to the observation in the oxidative benzene methylation with methane that the proportion of toluene relative to the amount of ethylbenzene, a secondary alkylation product, decreased over ZSM-5 catalysts on increasing the oxygen content since the increase in oxygen content would increase the yield of the methanol intermediate product of the reaction [3].

3.4. Effect of time on stream on catalytic performance

In all the different types of experiments investigated, benzene and methanol conversions and product selectivities on all the catalysts are generally found not to change significantly beyond 30 min on stream. This levelling of conversions and product selectivities beyond 30 min on stream may again be attributed to saturation of available Brönsted acid sites on the catalysts with increase in conversion levels during the course of the reaction. It is observed too that over the whole period of 105 min on stream, the selectivities to toluene are generally higher than selectivities to xylenes which in turn are higher than selectivities to other C_{9+} aromatics over the catalysts at any methanol/benzene molar ratio studied.

3.5. Anomalous behaviour of CuZSM-5

It is also observed in this work that the autoreduction behaviour of Cu(II) in CuZSM-5 [7] probably

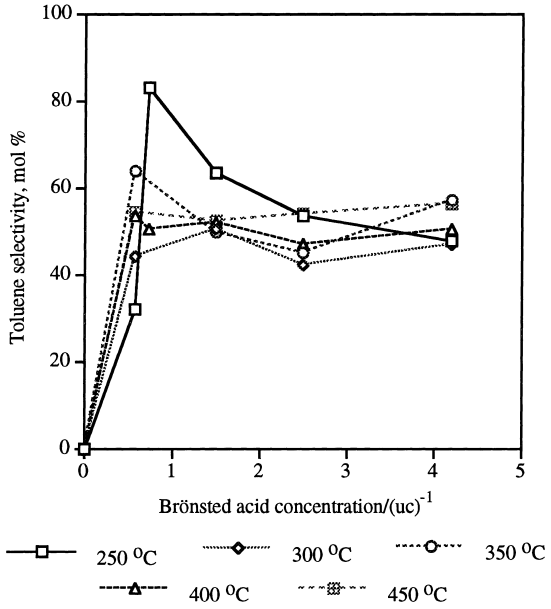

Fig. 4. Variation of toluene selectivity with Brönsted acidity at different temperatures (same reaction conditions as in Fig. 1).

makes CuZSM-5 to behave differently in certain ways. For example, in addition to the formation of significant amounts of diphenylmethane and bibenzyl at 250 and 300°C, methanol and benzene conversions on this catalyst are found to be exceptionally low compared to conversions on the other catalysts at these temperatures (Table 1 and Fig. 1). One explanation for the formation of large amounts of these high molecular weight compounds which needs to be confirmed by further investigation is the possibility of reduced copper sites to catalyse the coupling reactions of toluene and xylenes.

3.6. Conclusions

In conclusion, it is very clear that there is a excellent correlation between the performance of the zeolite catalysts for the methylation of benzene with methanol in a low pressure flow reactor and the methylation of benzene with methane in the presence of oxygen in a high pressure batch reactor. Also, a small number of Brönsted acid sites are observed to be necessary for both reactions. These results therefore provide further evidence to the two-step mechanism for the oxidative

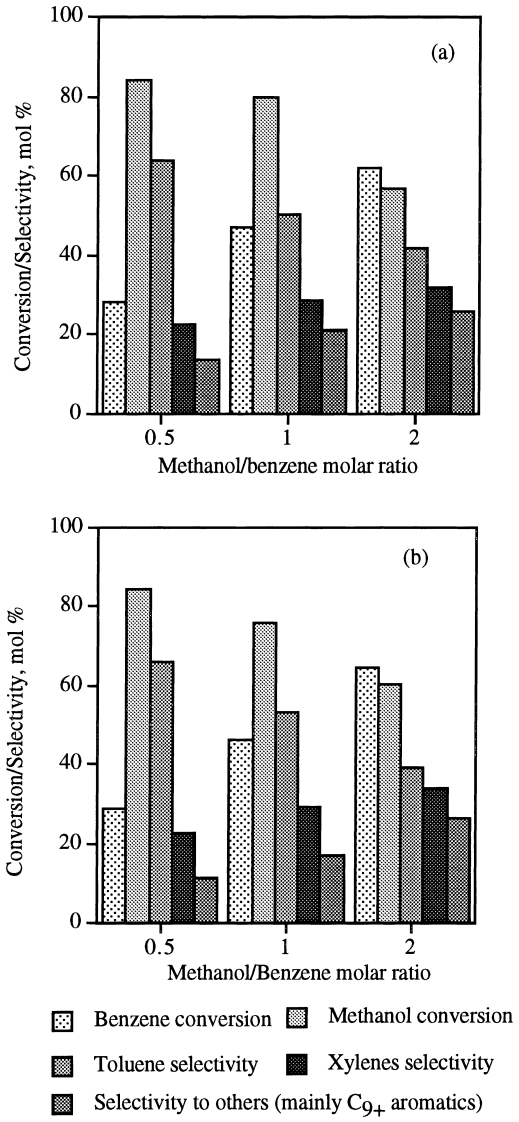

Fig. 5. Effect of varying methanol/benzene molar ratio on conversions and product selectivities at 400°C over (a) HZSM-5 and (b) CuZSM-5 (same reaction conditions as in Fig. 1).

benzene methylation reaction at 400°C in which the difficult homogeneous partial oxidation of methane to methanol is followed by facile methylation of benzene with methanol. Finally, the methanol to benzene molar ratio is observed to play some important role in the benzene methylation with methanol at 400°C and, in particular, higher yields of xylenes can be achieved by increasing this ratio.

Acknowledgements

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