Supplementary material

Effect of the crystal size of ZSM-11 zeolite on the catalytic performance and reaction route in methanol to olefins

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Table 1. Proportion of integrated peaks obtained by deconvolution of the ^{27}Al MAS NMR spectra of various ZSM-11 zeolites.

Zeolite	Al_F (%)	Al_{EF} (%)	Aluminum distribution (%)			
			48.5 ppm	55.6 ppm	58.1 ppm	53.2 ppm
L-ZSM-11	98.7	1.3	6.8	39.3	8.2	45.7
M-ZSM-11	98.3	1.7	8.5	37.6	8.9	45.0
S-ZSM-11	96.2	3.8	2.8	47.9	2.8	46.5

Al_F and Al_{EF} represent the percentages of Al atoms in the framework and extra-framework, respectively, obtained as the relative intensity of the signals at 45-65 and 0 ppm, respectively, in the ^{27}Al MAS NMR spectra. The proportions of various peaks were obtained by dividing their intensity by the total intensity of the signals in the range of 45-65 ppm. The peaks at 48.5, 55.6, and 58.1 ppm correspond mainly to Al atoms at T3, T4 + T6, and T5 sites, respectively, which are located in the intersection cavity, whereas the peak at 53.2 ppm represents the Al atoms at T1 + T2 + T7 sites in the straight channel.

Table 2. Catalytic results of various ZSM-11 zeolites in MTO.

Zeolite	x_M (%)	Product distribution (%)								(P−E)/E	2-MB/E	TON ×10^5	Lifetime
		C_1^0	C_{2-}	$C_2^=$	$C_3^=$	$C_4^=$	$C_5^=$	C_{6+}	arom				
L-ZSM-11	99.9	1.5	6.1	7.8	39.	26.1	10.	3.7	5.1	4.1	0.8	1.1	74
M-ZSM-11	99.9	1.3	5.5	5.6	41.	26.4	12.	4.0	3.4	6.5	1.3	1.9	134
S-ZSM-11	99.9	1.2	5.3	4.9	42.	26.5	12.	4.1	2.7	7.7	1.6	3.5	243

Methanol conversion and product distribution are provided at the half lifetime; C_1^0, $C_{2\text{-}5}^0$, $C_2^=$, $C_3^=$, $C_4^=$, $C_5^=$, C_{6+}, and arom. represent methane, ethane to pentane, ethene, propene, butene, pentene, aliphatics higher than pentane/pentene, and the sum of aromatics (benzene, toluene, xylene, and trimethylbenzene), respectively. (P-E)/E and 2-MB/E are the selectivity ratios of ([propene]-[ethene])/[ethene] and ([2-methylbutane] + [2-methyl-2-butene])/[ethene], which are used as indicators for the relative contribution of the alkene cycle to the aromatic cycle[1-4]. The turnover numbers (TONs) were determined by the accumulated number of methanol molecules converted per Brønsted acid site throughout the

whole lifetime [5].

Table 3. Catalytic performance of various ZSM-11 zeolites in MTO at sub-complete conversion of methanol.

Zeolite	WHSV (h^{-1})	Con. (%)	Product distribution (%)					(P−E)/E	2MB/E
			$C_2^=$	$C_3^=$	C_4-C_6	arom.	others		
L-ZSM-11	19.0	18.8	11.6	37.4	45.3	3.7	2.0	2.2	0.9
M-ZSM-11	9.5	16.1	8.2	39.7	47.9	2.0	2.2	3.8	1.3
S-ZSM-11	8.7	19.1	4.8	41.2	51.6	0.7	1.7	7.6	2.5

$C_2^=$, $C_3^=$, C_4-C_6, and arom. represent ethene, propene, C_4-C_6 aliphatics, and the sum of aromatics (benzene, toluene, xylene, and trimethylbenzene), respectively.

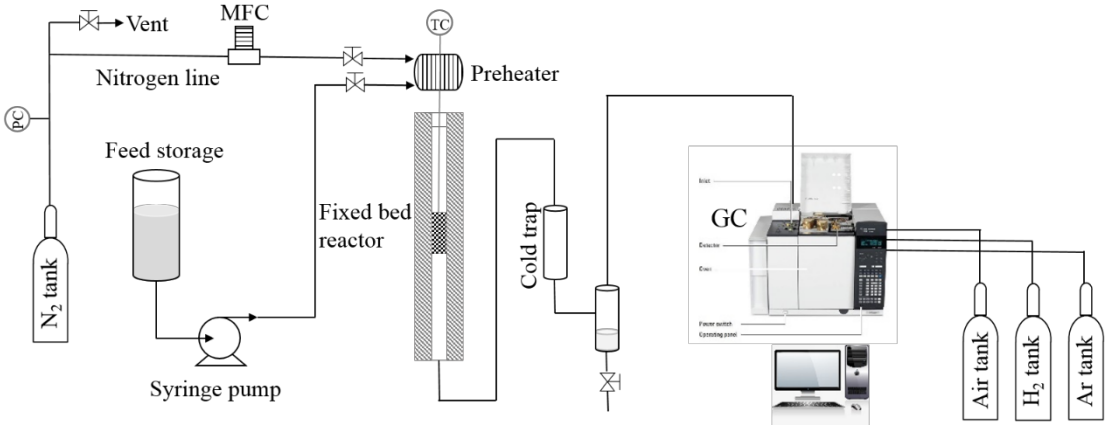

Figure 1. Schematic diagram of the catalytic evaluation system for the conversion of methanol to olefins (MTO).

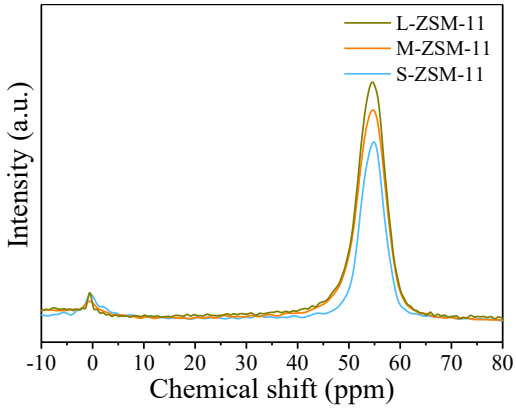

Figure 2. ^{27}Al MAS NMR spectra of L-ZSM-11, M-ZSM-11, and S-ZSM-11 zeolites.

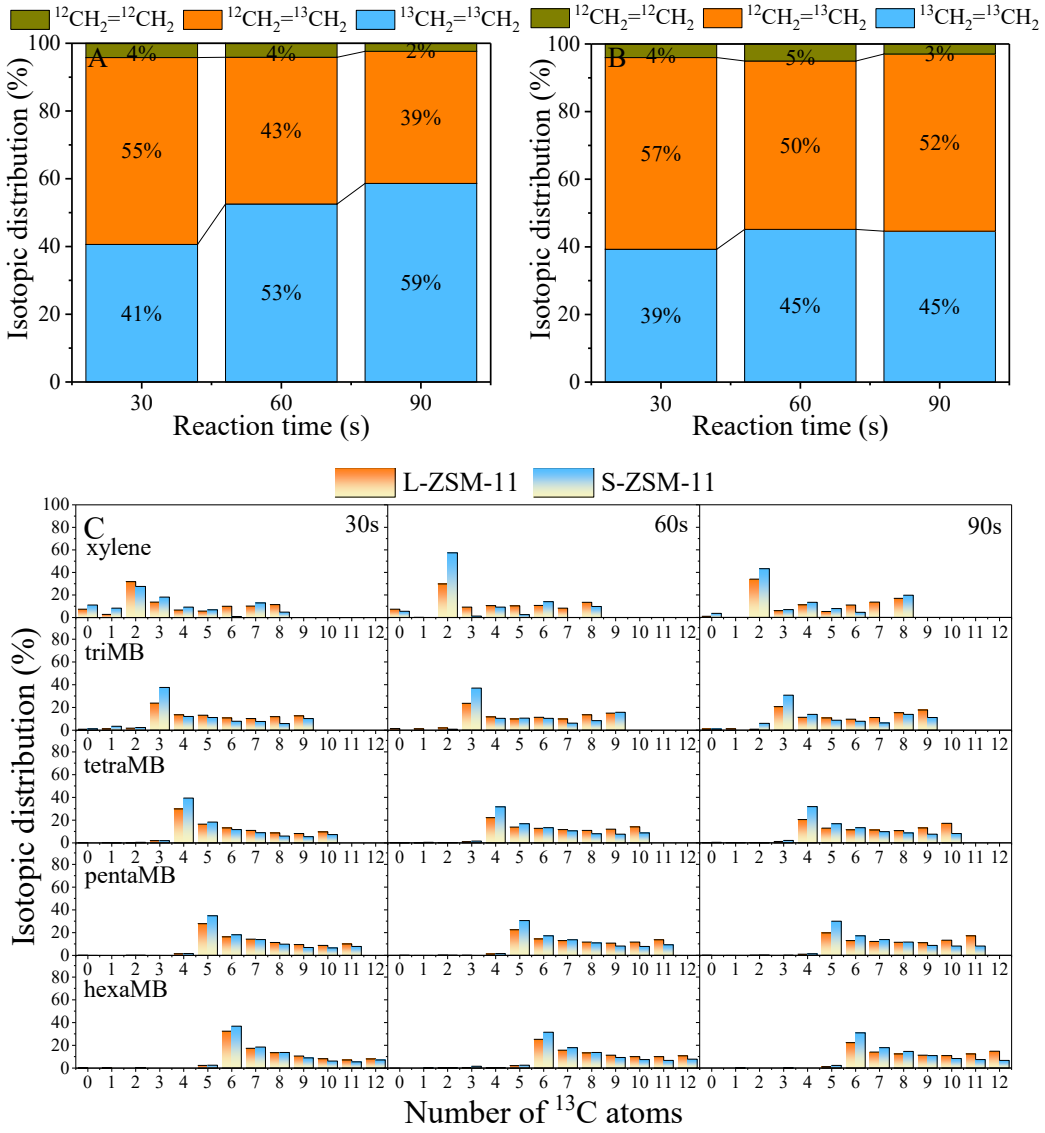

Figure 3. Distribution of ^{13}C atoms in ethene over L-ZSM-11 (A) and S-ZSM-11 (B) and (C) isotopic labeling patterns of retained polyMBs (xylene to hexa-MB) after different reaction times of co-reacting ^{13}C-methanol with ^{12}C-benzene (molar ratio 10.8:1) at 350 °C.

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