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Highly Efficient P-Modified HZSM-5 Catalyst for the Coupling Transformation of Methanol and 1-Butene to Propene

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A series of HZSM-5 zeolites modified by different amounts of phosphorus (P/HZSM-5) were prepared, and their catalytic performances for the coupling reaction of methanol and C4 hydrocarbons to light olefins were investigated. The results indicated that P/HZSM-5 is a highly efficient catalyst for the transformation of methanol and 1-butene to propene with low-energy consumption. At the temperature of 550 °C, the maximum yield of propene was achieved at 44.0%, which was 7.4 and 4.5% higher than those on 1-butene catalytic cracking and methanol to olefins (MTO), respectively. X-ray photoelectron spectroscopy (XPS) characterization on the catalyst showed that P bonds to the HZSM-5 zeolite framework through oxygen. The enhanced coupling performances can be correlated to the combined effects of matching of the co-feedings and the suitability of the P/HZSM-5 catalyst.

1. Introduction

Propene is the building block of the petrochemical industry. It is used as a feedstock for the production of a wide variety of important monomers, polymers, and chemicals, such as polypropylene, acrylonitrile, acrylic acid, propylene oxide, glycol, etc.¹ Recently, driven by the increasing demand for propene derivatives, the research on enhancing the production of propene has attracted more and more interest. At present, propene is mainly produced by steam cracking and fluid catalytic cracking (FCC). However, in the two processes, propene acts as the byproducts, which determine its low yield and the limited capability in boosting potential.² To cope with this, other techniques using hydrocarbons as raw materials for the production of propene include dehydrogenation of propane,³ the metathesis of ethene and butenes,⁴ the catalytic cracking of hydrocarbons,^{5–9} etc. Among them, the technique for the catalytic cracking of C4 hydrocarbons, because of its less valuable and abundant supply of feedstock, relatively low reaction temperature, and high selectivity to aimed products,

has been considered as an attractive alternative to produce propene.^{10,11}

From another view, with the petroleum resources lacking and the increasing of the world oil price, using a nonpetroleum resource for the production of light olefins has raised increasing interests, in which methanol to olefins (MTO) is most widely investigated.^{12–14} MTO is an exothermic reaction, while the catalytic cracking process is endothermic. The two reactions are based on an acid-catalyzed process, and the target products are both light olefins. From the viewpoints of the energy balance and target products, coupling the exothermic MTO with the highly endothermic hydrocarbon cracking reaction could obtain thermoneutral and, consequently, lower energy consumption. In this context, coupled methanol hydrocarbon cracking (CMHC) was proposed by Nowak and co-workers.¹⁵ In the CMHC process, several kinds of hydrocarbons including liquid and gaseous ones with methanol were investigated and HZSM-5 zeolites with different pretreatment and modification by transition metals were found suitable catalysts.¹⁶ Gao et al.^{17,18} studied the coupled reactions of propane/C4 hydrocarbons and methanol to aromatics and lower olefins over Ga/HZSM-5. Liu et al.^{19,20}

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investigated the coupling transformation of *n*-hexane and methanol over HZSM-5 and found that intermediate species and alkenes evolved from MTO help to promote the activation and conversion of *n*-hexane.

Thus far, the previous research on coupling transformation of hydrocarbons and methanol mainly focused on the optimization of the reaction conditions and modifications of the catalysts. Despite these remarkable achievements, to match the activation and reaction temperatures for the two different feedstocks of the coupling reaction is still the major challenge for further enhancing the coupling efficiency. To achieve this, several important methods are included as follows: (1) Selection of a suitable hydrocarbon for coupling, because the activation and cracking temperatures of hydrocarbons are often higher than those of methanol, from the view of the structural characteristics of the hydrocarbons, to choose a hydrocarbon that is easy to crack is desirable. (2) Design of effective catalysts with suitable pore structures and acidic properties. Studies have shown that HZSM-5 zeolite is suitable for this reaction, and further modification on parent HZSM-5 with suitable elements is very important. (3) Investigation and finding the optimized reaction conditions. With these thoughts in mind, we have investigated the coupling reaction performance of different kinds of C4 hydrocarbons (butanes and butenes) with methanol (including different molar ratios) on several modified HZSM-5 catalysts and found that the coupling of C4 alkenes with methanol (1:1) on P-modified HZSM-5 is the most efficient one. Although P-modified HZSM-5 has been investigated in hydrocarbon catalytic cracking^{11,21,22} and MTO,²³ respectively, the study of it in coupled reactions especially in the coupling transformation of methanol and 1-butene is seldom reported. According to our results, at the temperature of 550 °C, the propene yield of 44.0% was achieved, which was 7.4 and 4.5% higher than those on 1-butene catalytic cracking and MTO, respectively. To the best of our knowledge, this is the highest yield of propene that was obtained for CMHC. Such a result presents a good strategy for obtaining more light olefins with low energy consumption by improving the coupling efficiency of the reaction.

2. Experimental Section

2.1. Catalyst Preparation. The series of P/HZSM-5 catalysts were prepared as described previously.¹¹ HZSM-5 zeolite (Si/Al₂ ratio of 25, purchased from the catalyst company of NanKai University) was impregnated with an aqueous solution of (NH₄)₂HPO₄ by an incipient-wetness impregnation method. The mass fraction ratios of phosphorus to HZSM-5 zeolites were 0.1, 0.5, 1, 3, and 6%, respectively. The impregnation period lasted for an hour in the temperature range of 30–40 °C, then dried at 120 °C, and finally, calcined at 500 °C in an air atmosphere for 4 h. After finishing the preparation of the catalysts, they were marked as 1, 2, 3, 4, and 5 according to the different concentrations of P, correspondingly, and the HZSM-5 parent sample calcined at 500 °C in an air atmosphere for 4 h was marked as 0. The samples were pressed and crushed to particles of 40–80 mesh for catalytic testing and characterization.

2.2. Catalytic Activity Measurement. 1-Butene (obtained from Yanshan Petrochemical Company, Sinopec) and methanol (from

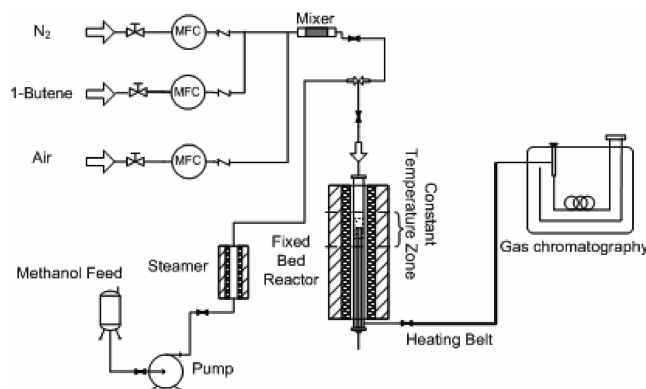


Figure 1. Schematic diagram of the experimental setup.

Table 1. Yields of Main Products for Catalytic Cracking of 1-Butene on P/HZSM-5 Catalysts

sample	temperature (°C)	yield (%)						
		CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₂ = + C ₃ =	BTX ^a
0	500	2.2	20.9	2.6	17.9	15.7	38.8	23.9
	550	4.3	30.1	3.5	20.4	6.4	50.5	28.8
	600	6.9	32.9	3.8	14.8	1.6	47.7	34.1
1	500	1.3	24.7	2.2	33.0	3.7	57.7	16.8
	550	3.0	32.4	3.1	27.7	3.7	60.1	19.5
	600	6.2	37.5	3.6	20.6	2.0	58.1	24.9
2	500	1.0	23.3	1.9	33.1	3.8	56.4	13.9
	550	2.6	30.7	2.6	29.4	3.4	60.1	17.3
	600	5.8	34.7	3.3	20.3	1.8	55.0	25.6
3	500	0.1	26.3	1.8	36.6	4.0	62.9	11.4
	550	1.7	31.4	2.6	35.6	4.0	67.0	12.7
	600	5.0	35.7	3.0	26.2	2.4	61.8	20.7
4	500	0.1	7.3	0.4	29.8	2.2	37.1	1.4
	550	0.8	10.2	0.6	28.4	2.2	38.6	2.0
	600	3.4	12.9	1.0	27.1	1.7	40.0	4.8
5	500	0.1	0.4	0.0	2.4	0.1	2.8	0.0
	550	0.5	1.0	0.1	3.4	0.1	4.4	0.0
	600	2.9	4.2	0.4	10.0	0.4	14.2	0.0

^a BTX included benzene, toluene, and xylene.

Beijing Chemical Reagents Company), with the molar ratio of 1:1, were used as feeds for the investigations. The coupling reaction was carried out in a fixed-bed microreactor system (Figure 1) by passing a gaseous mixture of 1-butene and methanol in a N₂ flow at a flow rate of 38 mL min⁻¹ over 300 mg of catalyst. The products were analyzed online using a gas chromatograph (SP-2100) equipped with a 50 m PONA capillary column and a flame ionization detector (FID).

2.3. Catalyst Characterization. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon.

3. Results and Discussion

3.1. Catalytic Performances of P/HZSM-5 for the Cracking of 1-Butene. Table 1 presents the distribution of main products for the catalytic cracking of 1-butene on P/HZSM-5 catalysts. From Table 1, it can be seen that, on all of the catalysts from 0 to 5, the yields of methane and BTX show increasing trends with increasing the reaction temperatures. At the same temperatures, the yields of methane and BTX decrease with enhancing the loading amount of phosphorus. In addition, at the temperature of 600 °C, the highest yield of BTX on the P-modified HZSM-5 sample (2) was 25.6%,

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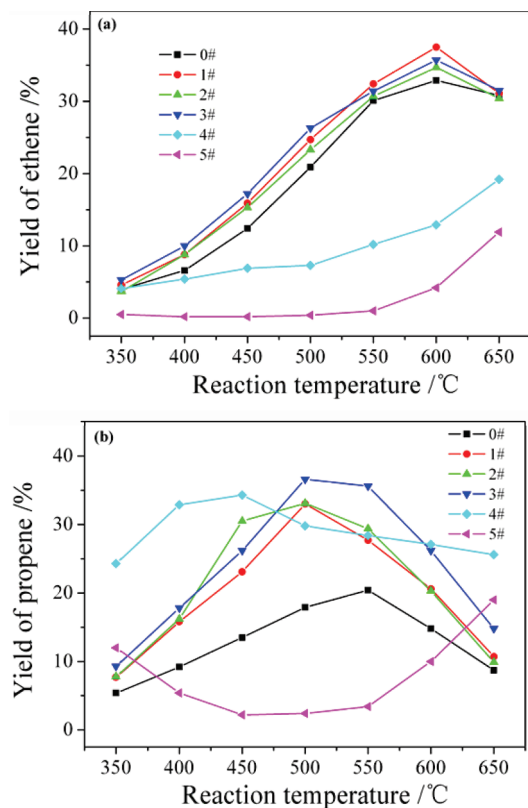


Figure 2. Yields of (a) ethene and (b) propene over P/HZSM-5 as a function of the temperature for the 1-butene catalytic cracking reaction.

which was 8.5% lower than that on parent HZSM-5. Our previous research¹¹ showed that P modification on HZSM-5 decreased the percentage of strong acidic sites in total acidic sites, which decreases the selectivity to aromatics because of the lowered activity of the strong acids on the secondary reactions of olefins, such as hydrogen transfer, etc.^{2,24} In the studied temperature range, the yields of ethane and propane were relatively low.

Figure 2 shows the yields of ethene and propene in the catalytic cracking of 1-butene over parent and P-modified HZSM-5 catalysts. From Figure 2a, it can be seen that, at the temperatures lower than 600 °C, the yield of ethene increased with increasing the reaction temperatures. Among the six studied catalysts, the P-modified 1 sample was optimal for the production of ethene. At the temperature of 600 °C, the highest yield of ethene was obtained 37.5%, which was 4.6% higher than that on parent HZSM-5. Different from the trends on ethene, the yield of propene shown in Figure 2b increased first and then decreased with further increasing the reaction temperature. This is due to the fact that, for the catalytic cracking reaction, propene is the intermediate product. Further increasing the reaction temperature will facilitate the secondary reactions and, consequently, lower its yield. In addition, P modification demonstrated its effectiveness for the enhanced production of propene, at the temperature of 500 °C, and the highest yield of propene was achieved 36.6% over the 3 sample, which was 16.2% higher than that on parent HZSM-5.

Table 2. Yields of Main Products for the MTO Reaction on P/HZSM-5 Catalysts

sample	temperature (°C)	yield (%)						
		CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₂ = + C ₃ =	BTX ^a
0	450	19.8	10.7	1.9	13.2	6.7	23.8	20.9
	500	21.0	20.5	2.9	14.5	8.2	35.0	27.6
	550	22.2	18.0	2.3	8.3	2.8	26.3	25.0
	600	49.2	12.7	2.4	3.0	0.5	15.7	22.4
1	450	2.7	15.4	1.6	19.9	11.9	35.2	15.3
	500	5.2	24.0	2.2	22.8	7.6	46.8	15.9
	550	8.7	29.6	3.2	18.3	4.7	48.0	19.3
	600	17.4	25.5	2.6	10.5	1.9	36.0	26.9
2	450	3.6	15.0	1.5	22.4	9.4	37.5	14.8
	500	8.5	22.7	2.3	22.9	8.5	45.6	18.2
	550	13.6	26.4	2.9	16.0	5.1	42.4	24.5
	600	25.3	18.9	2.6	8.0	1.5	26.9	28.8
3	450	3.4	17.1	1.5	25.3	7.8	42.4	12.2
	500	4.9	26.4	2.1	28.8	6.4	55.3	13.9
	550	6.1	29.8	3.3	25.4	5.7	55.2	15.4
	600	12.0	26.3	2.4	18.5	2.7	44.8	20.2
4	450	1.1	6.1	0.6	32.5	6.1	38.6	2.0
	500	1.1	8.8	0.8	39.5	7.5	48.4	1.9
	550	1.6	10.0	1.0	37.2	7.7	47.1	2.0
	600	3.2	11.0	0.8	32.6	5.3	43.6	2.2
5	450	1.0	1.0	0.1	0.8	0.1	1.8	0.0
	500	3.1	2.6	0.3	1.8	0.2	4.4	0.0
	550	5.4	4.4	0.4	2.5	0.2	6.9	0.0
	600	8.4	3.5	0.6	1.6	0.2	5.1	0.0

^a BTX included benzene, toluene, and xylene.

3.2. Catalytic Performances of P/HZSM-5 for MTO Reaction. Table 2 presents the yields of the main products for the reaction of MTO. From Table 2, it can be seen that the yields of methane and BTX increased with increasing the reaction temperature and decreased with enhancing the loading of P. At the temperature of 600 °C, the maximum yield of methane reached 49.2% on parent HZSM-5, indicating that, at higher temperatures, a large fraction of methanol converted into methane. In contrast, on the P-modified HZSM-5 catalyst, with the reaction temperatures lower than 550 °C, the yields of methane and BTX were greatly decreased, especially on the HZSM-5 with a higher loading of P. The yield of ethane increased first and then decreased with increasing the reaction temperatures, and in the studied temperature range, it was kept low. The yield of propane decreased with increasing the reaction temperatures.

Figure 3 shows the yields of ethene and propene in the MTO reaction over parent and P-modified HZSM-5 catalysts. From Figure 3a, it can be seen that, with the temperatures lower than 550 °C, the yields of ethene increased with increasing the reaction temperatures. For P modification, two cases occurred. With the loading of P lower than 1%, P modification is helpful for the formation of ethene and higher yields of ethene were obtained than that on the unmodified sample. While on HZSM-5 with P content higher than 1%, lower yields of ethene were obtained. Similar to the trend of propene in 1-butene catalytic cracking, the yield of propene shown in Figure 3b increased first and then decreased with increasing the reaction temperatures. Except for the 5 catalyst, the yield of propene increased with increasing P loadings. In addition, the maximum propene yield reached 39.5% over the 4 catalyst at 500 °C, which was 25.0% higher than that on HZSM-5.

3.3. Catalytic Performances of P/HZSM-5 for the Coupling Reaction of Methanol and 1-Butene. Table 3 presents the distributions of the main products for the coupling

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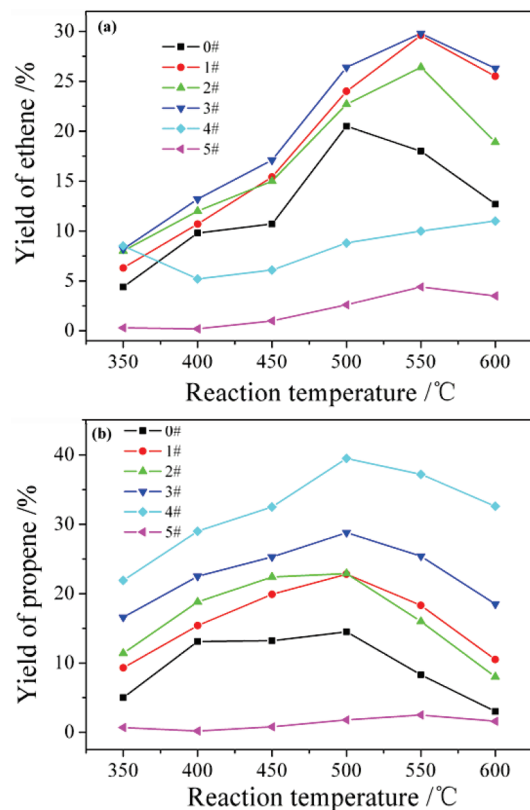


Figure 3. Yields of (a) ethene and (b) propene over P/HZSM-5 as a function of the temperature for the MTO reaction.

Table 3. Yields of Main Products for the Coupling Reaction of Methanol and 1-Butene (Molar Ratio of 1:1) on P/HZSM-5 Catalysts

sample	temperature (°C)	yield (%)						
		CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₂ = + C ₃ =	BTX ^a
0	500	7.7	14.7	3.9	15.0	13.3	29.7	26.2
	550	10.4	21.7	4.4	17.5	5.7	39.2	26.0
	600	15.6	24.2	3.7	13.6	1.6	37.7	28.0
	650	25.6	19.8	3.3	7.6	0.8	27.5	26.8
1	500	5.0	15.6	4.0	18.9	10.1	34.5	27.0
	550	9.3	21.8	5.1	18.5	5.1	40.3	26.8
	600	16.1	22.9	4.3	12.2	1.4	35.1	28.1
	650	28.9	18.7	3.4	5.9	0.6	24.7	27.0
2	500	4.4	19.2	2.7	22.8	11.6	42.0	20.1
	550	7.0	24.9	3.5	20.9	6.4	45.9	22.2
	600	11.6	28.9	3.6	16.8	2.5	45.7	24.7
	650	20.7	25.1	3.1	9.6	0.8	34.7	25.0
3	500	3.9	21.5	2.2	29.3	6.8	50.8	16.1
	550	5.4	28.7	3.0	29.2	4.1	57.8	17.4
	600	9.3	33.4	3.6	23.5	2.8	56.9	19.4
	650	21.6	30.8	3.6	15.0	1.5	45.8	20.9
4	500	0.8	8.9	0.6	39.5	3.5	48.3	1.7
	550	1.4	12.7	0.8	44.0	2.7	56.7	1.8
	600	4.7	13.4	1.1	39.4	1.3	52.8	3.1
	650	16.8	14.1	1.8	26.7	1.7	40.8	4.2
5	500	1.2	0.6	0.1	1.0	0.1	1.6	0.0
	550	1.5	0.8	0.2	2.4	0.1	3.2	0.0
	600	3.8	2.3	0.4	6.9	0.3	9.2	0.0
	650	16.2	9.4	1.5	1.1	0.4	10.5	0.0

^a BTX included benzene, toluene, and xylene.

transformation of methanol and 1-butene (1:1). From Table 3, it can be seen that, at temperatures lower than 600 °C, the yield of methane was low. Except for sample 5, the catalysts demonstrated good performances for obtaining

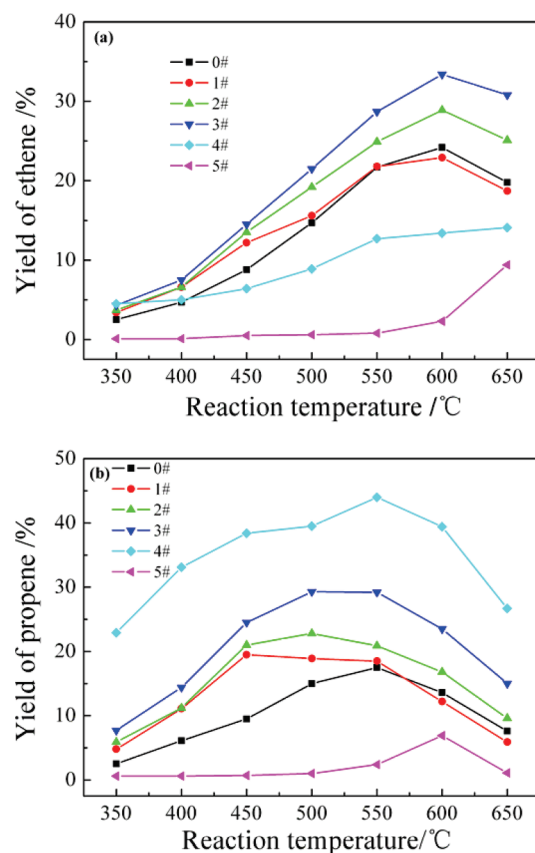


Figure 4. Yields of (a) ethene and (b) propene over P/HZSM-5 as a function of the temperature for the coupling reaction of methanol and 1-butene.

ethene plus propene. Among the catalysts, sample 3 is good for the production of ethene and sample 4 helps to obtain more propene. The yield of propane decreased with increasing the reaction temperature, and the yield of ethane showed no obvious changes with varying the reaction temperature. In the studied temperature range, the two products of ethane and propane accounted for small proportions of the main products. The yield of BTX decreased with increasing the loading of P, especially when the content of P was more than 1% (3 sample), indicating that HZSM-5 zeolite with higher loadings of P helps to prohibit the formation of BTX for the coupling reaction.

Figure 4 shows the yields of ethene and propene in the coupling reaction of methanol and 1-butene over parent and P-modified HZSM-5 catalysts. From Figure 4a, it can be seen that, with P loading lower than 1% (3), the yield of ethene increased with an increasing P loading. Further increasing the content of P on HZSM-5 led to the decrease of the yield of ethene. At the temperature of 600 °C, the highest ethene yield of 33.4% was achieved on the 3 sample. The yield of propene with reaction temperatures in the coupling reaction of methanol and 1-butene showed that P-modified HZSM-5 is a good catalyst for the production of propene. Except for the 5 sample with the maximum P loading by 6%, the yield of propene over P-modified HZSM-5 was obviously higher than that over unmodified HZSM-5, and it increased with increasing the loading of P. At the temperature of 550 °C, the maximum propene yield reached 44.0% over the 4 sample, which was 4.5% higher than that for the MTO reaction and 7.4% higher than that

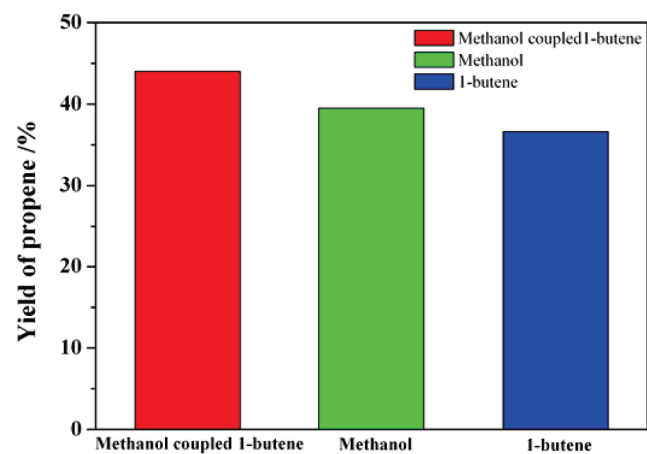


Figure 5. Yields of propene for the CMHC, MTO, and 1-butene catalytic cracking reaction.

for the catalytic cracking of 1-butene (Figure 5). To the best of our knowledge, this is the highest yield of propene that was obtained for CMHC. According to our previous research on the same series of the P/HZSM-5,¹¹ the proportion of the weak acid amount in the total acid amount of P/HZSM-5 increased with the increase of the loading of P, while excessive P loading (6%) on the 5 catalyst led to the loss of Brunauer–Emmett–Teller (BET) surface area and the acid site concentrations by pore blockage. Among the samples, although the 4 sample does not possess the largest amount of weak acid nor the largest BET surface area, it simultaneously possesses the larger weak acid amount and a certain BET surface area. When this is combined with the fact that the optimal yield of propene is achieved on the 4 sample, it can be concluded that a larger proportion of weak acid in total acid with a suitable BET surface area of the present catalyst is important for obtaining more propene for the CMHC reaction. In comparison, the coupling effect did not occur in the coupling reaction of methanol and mixed C4 hydrocarbons (including butanes and butenes) on the P-modified HZSM-5 catalyst (see Tables S1 and S2 in the Supporting Information). It is estimated that C4 alkanes in the mixed C4 hydrocarbons are more difficult to crack than C4 alkenes, and they need higher temperatures for activation, leading to the temperature difference and mismatch between the two feedstocks of the reaction. All of this demonstrated the effectiveness of the coupling of methanol and 1-butene as well as the suitability of P modification for this reaction.

To investigate the stability of the P/HZSM-5 catalyst, the catalytic test was performed on the 4 sample at 550 °C. The results in Table 4 show that the yields of methane and BTX are kept low, indicating that the present catalyst can promote the generation of light olefins by inhibiting the byproduct generation of methane and BTX. From Table 4, it can also be seen that there was a decrease in the yield of propene and/or ethene after 10.0 h of continuous reaction. During the process of the experiment, it can be found that the majority of methanol converts into C4 hydrocarbons when the reaction time is longer than 0.2 h. It is known that the long time reaction brings about the coking of the catalyst, and the coking occurs on the acid sites. The reduced amount of the acid sites resulted in the sharp decrease in the yield of propene. After burning off the coke, the catalyst was regenerated and the yields of ethene and propene were restored.

Table 4. Yields of Main Products for the Coupling Reaction of Methanol and 1-Butene as a Function of the Reaction Time over the 4 Catalyst at 550 °C before and after Regeneration

reaction time (h)	yield (%)						
	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₂ = + C ₃ =	BTX ^a
0.2	2.5	13.3	0.9	44.2	2.3	57.5	3.3
1.0	2.8	8.8	0.8	38.7	2.7	47.6	2.7
2.0	3.5	8.1	0.6	37.4	2.4	45.4	2.7
3.0	3.8	7.3	0.6	37.6	2.4	44.9	2.7
4.0	4.0	6.5	0.6	34.7	2.4	41.2	2.6
5.0	4.7	5.9	0.6	33.3	2.1	39.3	2.0
6.0	4.4	5.2	0.5	31.1	1.8	36.3	2.3
7.0	5.1	5.2	0.5	31.4	1.7	36.6	2.4
8.0	4.9	4.6	0.5	27.2	1.7	31.8	2.1
9.0	4.6	4.1	0.4	24.5	1.5	28.6	2.6
10.0	5.0	4.1	0.5	24.1	1.4	28.2	2.8
after Burning off the Coke							
0.2	3.1	16.0	1.2	40.3	2.7	56.3	4.9

^a BTX included benzene, toluene, and xylene.

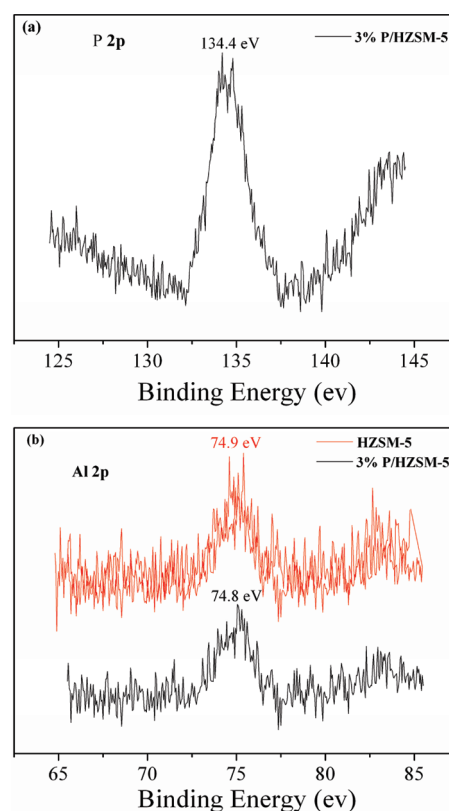


Figure 6. XPS spectra for the regions of (a) P 2p and (b) Al 2p.

3.4. XPS of P/HZSM-5 Catalysts. XPS measurements were performed to study the interaction between P and the HZSM-5 zeolite surface. Before modification, P existed in the form of HPO_4^{2-} and its binding energy was about 132.7 eV.²⁵ Figure 6a shows the recorded spectrum P 2p peak of P/HZSM-5. After modification, the binding energy of phosphorus shown in Figure 6a shifted to 134.4 eV. According to the literature on different P compounds as a function of the number and nature of the attached ligands,²⁵ it was

(25) Wagner, C. D.; Riggs, W. M.; Davis, L. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Eden Prairie, MN, 1979.

concluded that P bonds to the HZSM-5 zeolite framework through oxygen. This may come from the fact that the bridging hydroxyl groups of the zeolite were partly substituted by the phosphorus hydroxyl (P–OH) after modification.^{22,26} The Al 2p binding energies shown in Figure 6b were observed at 74.9 and 74.8 eV for HZSM-5 before and after P modification. Such results suggest that some electrons shifted from P to Al via oxygen, which is consistent with the increase of the binding energy of P 2p.

4. Conclusions

A series of HZSM-5 zeolites modified by different amounts of phosphorus were prepared, and their catalytic performances for the coupling reaction of methanol and C4 hydrocarbons to light olefins were investigated. The results indicated that, after modification, P attached to the HZSM-5 zeolite framework via oxygen and the P-modified HZSM-5 catalyst showed better catalytic performances for the MTO, catalytic cracking, and coupling reactions. Among the different co-feedings of the coupling reactions, the coupling of methanol and 1-butene on P/HZSM-5 demonstrated a prominent coupling effect. At the temperature of 550 °C, the

maximal propene yield of 44.0% was achieved, which was 7.4 and 4.5% higher than those on 1-butene catalytic cracking and MTO, respectively. Such a result was attributed to the integrated effects of the matching of the co-feedings and suitable modification of HZSM-5 zeolite and presents a good strategy for obtaining more light olefins with low-energy consumption by improving the coupling efficiency of the reaction.

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Supporting Information Available: Yields of main products for the catalytic cracking of mixed C4 hydrocarbons on P/HZSM-5 catalysts (Table S1), yields of main products for the coupling reaction of methanol and mixed C4 hydrocarbons (molar ratio of 1:1) on P/HZSM-5 catalysts (Table S2), and yields of main products for the coupling reaction of methanol and 1-butene (molar ratio of 3:1) on P/HZSM-5 catalysts (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(26) Blasco, T.; Corma, A.; Martínez-Triguero, J. *J. Catal.* **2006**, *237*, 267–277.