Applied Catalysis A: General 374 (2010) 18–25

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Novel aluminophosphate (AlPO) bound ZSM-5 extrudates with improved catalytic properties for methanol to propylene (MTP) reaction

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ARTICLE INFO

Article history:
Received 8 June 2009
Received in revised form 12 November 2009
Accepted 16 November 2009
Available online 20 November 2009

Keywords:
Aluminophosphate
ZSM-5
Acidity control
Mechanical strength
MTP

ABSTRACT

Novel aluminophosphate (AlPO) binders consisting of dense phases of alpha-cristobalite and tridymite were prepared by the treatment of pseudo-boehmite (AlO(OH)) with phosphoric acid. The ZSM-5 extrudates prepared by using AlPO binders have been characterized by XRD, N_2 sorption, NH_3-TPD, ^{27}Al and ^{31}P NMR techniques to elucidate the changes that occurred in the textural properties of the catalyst and their implications on the catalytic activity of the resultant ZSM-5-based extrudates towards methanol to propylene (MTP) reaction. XRD indicated the chemical interaction of P with the alumina binder to form a highly dense crystalline phase of aluminophosphate, alpha-cristobalite. N_2 adsorption, while NH_3-TPD studies revealed the changes in pore morphology of AlO(OH) binder and acidity of ZSM-5 in phosphorus containing extrudates. The drastic decrease in mesoporosity of the AlO(OH) observed after phosphorus addition indeed envisions the disappearance of inter-crystalline voids in the AlO(OH), probably due to a change in its morphology from the crystalline phase to amorphous AlPO phase. ^{27}Al and ^{31}P NMR studies further confirmed the formation of AlPO in these samples. The resultant ZSM-5-based extrudates exhibited enhanced properties of hydrothermal stability, mechanical strength, propylene yield and coke resistance in methanol to propylene (MTP) reaction. The positive aspect of P addition was continuously increased with P amount; at optimum P/Al (binder) ratio of ~0.8, the catalyst exhibited about 80% yield to C_2–C_4 olefins with the major component being propylene (~50%) at near 100% methanol conversion. The catalyst also exhibited the stable performance in the studied period of 150 h.

1. Introduction

The distinct acidity demonstrated by the systematic arrangement of silicon and aluminum tetrahedral units in zeolites provides a platform for a variety of hydrocarbon conversions to produce industrially important petroleum and petrochemical components such as olefins, iso-paraffins and aromatics. Conversion of methanol to light olefins especially propylene is gaining importance, due to its applications in the production of various petrochemicals. This reaction also provides an alternative source to traditional resources such as natural gas, coal and biomass, for the production of light olefins [1–3]. The well-known Lurgi process operates for the production of propylene from methanol, where gasoline, LPG and fuel gas appear as byproducts that limit the maximization of propylene yields in once-through operation. The hydro process of UOP/Norsk operates for the selective production of light olefins from methanol on a SAPO based catalyst [2,4]. But achieving high yields of propylene is still challenging. The classical representation for the reaction pathway of methanol conversion consists of several consecutive reaction steps initialized by the dehydration of methanol to dimethyl ether (DME), followed by its further dehydration to form light olefins, which are reactive enough to form several hydrocarbon end-products such as paraffins, oligomers, aromatics and even the coke precursors responsible for the catalyst deactivation [1]. Recent studies reveal a much clearer insight into the reaction aspects [5,6]. The key step in effective conversion of methanol to propylene lies in controlling the reaction at the olefin formation stage, where the acidity of the catalyst plays a vital role.

Variation of framework Si/Al ratio by pre or post synthesis methods is a generally adopted procedure for tuning the zeolite acidity. However, the powder form of zeolite needs to be shaped with the help of an inert binder material to achieve the mechanical strength required for using it in industrial reactors for catalytic applications [7,8]. The binder material used for shaping the zeolites is also observed to contribute to the acidity and porosity of the zeolites [9]. Though the binder is not active as a catalyst but can change the acid properties of the zeolite by altering its proton-exchange efficiency or by physical occupation of zeolite pores during the pelletization process [10,11]. For example, the aluminum in an

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doi:10.1016/j.apcata.2009.11.019

alumina binder can interact with zeolite to form additional acid sites [12,13]. In a similar way, the silica binders decrease the acidity of the protonic form of zeolites [14,15]. Clay such as Bentonite exhibits poor binding properties in its acidic form and hence needs to be used in alkali form for making extrudates, followed by the treatment of clay-zeolite agglomerates to their protonic form. This makes the process tedious [16]. Pseudo-boehmite is generally used as binder for the preparation of zeolite extrudates [17]. Modification of ZSM-5 acidity by loading phosphorus compounds viz. trimethylphosphite and phosphoric acid is observed to improve the catalytic properties of ZSM-5 [18,19]. Since, addition of binder material is obvious for achieving the desired mechanical strength and diluting the acid density of the ZSM-5, addition of P to the binder may have direct influence on the properties of binder and resultant extrudates. Few Studies are available on the incorporation of P into the binder material in the development of catalysts. Recently, Freiding et al. [20] used amorphous aluminophosphate hydrate as binder for preparation of ZSM-5 extrudates of improved properties. However, the materials have not been proven to be available for improved catalytic applications.

In the present study, the effects of P addition on the properties of AlO(OH) binder and on the properties of ZSM-5 extrudates have been studied, with special reference to its applications to the MTP reaction. The present study deals with the following aspects of the catalysts for MTP reaction:

1. Preparation of AlPO binder by the addition of various amounts of P to the pseudo-boehmite and shaping the ZSM-5 for extrudate preparation.
2. Effect of binder composition on mechanical strength, acidity, porosity and their implications on MTP reaction.
3. Hydrothermal stability, coke resistance and long time performance of catalysts.

Here we report the successful development of an AlPO binder based ZSM-5 catalyst exhibiting tuned properties of acidity for selective production of propylene manifested by the effective interaction of P with the AlO(OH) as well as with the ZSM-5 framework to produce as high as 45% propylene at near 100% conversion of methanol. The transformation of pseudo-boehmite crystalline phase into amorphous AlPO phase by P addition and its conversion into highly dense alpha-cristobalite with calcination gave exceptionally high mechanical strength to the catalyst even at lower binder (20 wt%) content in the extrudates. At optimized reaction conditions, the catalyst exhibited stable performance in the studied period of 150 h.

2. Experimental

2.1. Catalyst preparation

In order to change the properties of the AlO(OH) binder, we added P to the binder before mixing it with the zeolite for shaping. The amount of P in the binder is varied from P/Al mole ratio of 0.0–1.2. The catalyst preparation is made in two steps: (1) peptization of pseudo-boehmite by treatment with acid and (2) mixing the peptized binder with zeolite to obtain extrudates. Nitric acid and phosphoric acid are used as peptizing agents for the preparation of P-free and P-containing extrudates respectively. In a typical procedure, the ZSM-5 extrudates having aluminophosphate of P/Al = 1.0 mole ratio have been prepared by the following method: 6.55 g phosphoric acid is added to 3.86 g of pseudo-boehmite containing 11.7 g of water with constant stirring to obtain a well-mixed paste of aluminophosphate. This paste is then added to 24.9 g of ZSM-5 (Zeolyst CBV 8014, Si/Al = 40), followed by thorough mixing and extruding the resultant paste with a syringe of 2 mm inner diameter. The extrudates are dried at 110 °C followed by calcinations at 600 °C for 6 h. A similar procedure is applied to obtain the binder with varying P/Al molar ratios from 0.2 to 1.2. The samples prepared with varying phosphorus content were designated as ZAlPO$_x$, where *x* represents the P/Al molar ratio in the AlPO binder.

Some P-free alumina based ZSM-5 extrudates were also prepared by the same method except for the acid, where nitric acid is used in place of phosphoric acid for the treatment of pseudo-boehmite. The P-free bound ZSM-5 sample was designated as ZAl. Throughout the studies, the zeolite to binder ratio is kept at a constant value of 80:20 by wt%.

2.2. Characterization of the catalysts

The XRD patterns of the synthesized samples were recorded on a Rigaku D/MAX IIIB X-ray diffractometer with Cu Kα radiation. The surface acidity of the samples was measured by temperature programmed desorption of ammonia (NH_3-TPD) using a BEL-CAT PCI 3135 with TCD detector. In a typical analysis, 0.2 g of the calcined sample was pretreated at 500 °C for 3 h to remove adsorbed water and then saturated with ammonia at 100 °C for 1 h. After saturation, the sample was purged with helium for 30 min to remove the weakly adsorbed ammonia on the surface of the catalyst. The temperature of the sample was then raised from 100 to 700 °C at a heating rate of 10 °C min^{-1}. The curves obtained at two regions, 100–325 °C (I region, weak acid) and 325–580 °C (II region, strong acid) were integrated and calibrated with standard sample (NH_4–ZSM-5, 0.99 ± 0.1 mmol g^{-1}). BET surface area measurements and pore volume measurements were obtained from N_2 adsorption–desorption isotherms conducted at −196 °C using a TriStar 3000 (Micromeritics) instrument. Prior to the adsorption–desorption measurements, all the samples were degassed at 300 °C in vacuum for 4 h. Thermo-gravimetric analysis (TGA) was conducted on the spent catalysts to analyze coke amounts using a TA Instrument (DMA, SDT 2960), where the samples are heated up to 800 °C at a heating rate of 10 °C/min under controlled air flow (100 mL/min). The compressive mechanical strength of the cylindrical extrudates (6 mm diameter and 12 mm length) was measured using a Universal Testing Machine (UTM, Instron 4482) with 10 kN load cell at a crosshead speed of 0.1 mm min^{-1} until failure occurred.

Solid-state magic angle spinning (MAS) NMR experiments were performed on a Varian Unity INOVA 600 MHz (14.09 T) spectrometer with a 4 mm zirconia MAS probe at a rotation rate of 14 kHz. The ^{27}Al MAS NMR spectra were obtained at a Larmor frequency of 156.4 MHz using a short RF pulse length of 1.0 μs and a recycle delay of 2 s. Chemical shifts of the ^{27}Al spectra were referenced to [$Al(H_2O)_6^{3+}$] (0 ppm). The ^{31}P MAS NMR spectra were obtained at Larmor frequencies of 242.7 MHz using a short RF pulse length of 4.0 μs and a recycle delay of 8 s. Chemical shifts of the ^{31}P spectra were referenced to 85% H_3PO_4.

2.3. Catalytic activity

Catalytic activity of all the samples towards methanol conversion was measured in a fixed bed micro-reactor (316 stainless steel tubing, I.D. = 1 cm and length = 30 cm) at atmospheric pressure in the temperature range of 300–550 °C. The catalyst particles (1–2 mm size) were loaded into the reactor and activated at 500 °C for 1 h in a N_2 flow. Methanol feed containing 20 mol% H_2O was fed into the reactor with corresponding WHSV of 2.55 h^{-1}. N_2 as a diluent gas was co-fed with MeOH:N_2 ratio of 1:9 (v/v). The effluent gas from the reactor was analyzed by an online gas chromatograph (Donam GC 6100) employing GS-Q capillary columns for hydrocarbons and oxygenates, respectively. Product compositions were calculated based on a standard gas mixture.

3. Results and discussion

3.1. Changes in textural properties of pseudo-boehmite by P addition

X-ray diffraction patterns of the pseudo-boehmite binder before (Al) and after the P addition (AlPO) are given in Fig. 1. The parent binder (Al) after calcination exhibits the structure of gamma-alumina. As shown in Fig. 1, phosphorus addition to the pseudo-boehmite followed by its calcination changed the structure to the crystalline aluminophosphate phases of alpha-cristobalite and tridymite (AlPO 0.8). This change clearly envisions the effective interaction of P with the aluminum of pseudo-boehmite to form an entirely new chemical phase of aluminophosphate.

The MAS NMR results also support the interaction of P with the aluminum in the binder to form aluminophosphate (AlPO). The ^{27}Al NMR spectra of the P-containing and P-free extrudates are given in Fig. 2(a). The P-free ZSM-5 extrudates (ZAl) exhibit a signal at 53.8 ppm corresponding to the framework aluminum ($Al(OSi)_4$) of the ZSM-5. In addition, two signals at 69 and 8.7 ppm were also observed in the sample. These can be attributed to the aluminum present in the pseudo-boehmite in tetra-($Al(OAl)_4$) and hexa-coordination ($Al(OAl)_6$), respectively [21,22]. In phosphorus containing (ZAlPO) samples, the intensities of these two signals are decreased with P loading and they are almost disappeared at higher phosphorus loadings (ZAlPO 1.2). This is accompanied by the simultaneous formation of two new signals at 39 ppm and −13.7 ppm in ZAlPO samples; the intensities of these new signals are also increased with the P amount in the samples. Thus the signals that appeared in the present study clearly suggest the formation of $Al(OP)_4$ and $Al(OP)_6$ species by the interaction of P with the pseudo-boehmite in the P-loaded samples [22,23]. In addition the signal at 53.8 ppm is also decreased with the increase of P content in ZAlPO samples. The framework aluminum can be combined with phosphate to form aluminum species of ($Al(O\text{-}Si)_3(OP)$) where the signal of 53.8 ppm can shift to around 39 ppm which overlaps with the signal of binder $Al(OP)_4$ [24].

The interaction between phosphorus and aluminum was also reflected in ^{31}P NMR (Fig. 2(b)), where the P-containing samples (ZAlPO) exhibited a band at −31 ppm representing the $P(OAl)_4$ species. At lower P loadings, the band is broad; the sharpness of the signal is increased with the P amount. This observation along with ^{27}Al supports the interaction of P with the binder aluminum. At higher P loadings, the samples also exhibited the low energy signals at 6, −6.3 and −45 ppm representing the formation of minute amounts of pyrophosphate and polyphosphate species [22,23].

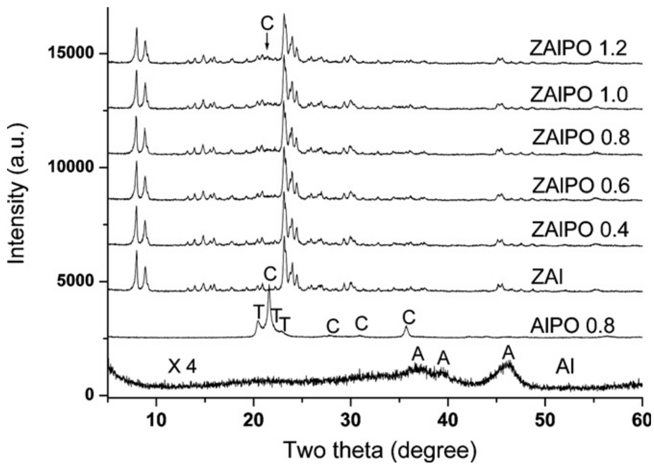

Fig. 1. X-ray diffraction patterns of binder and bound zeolite samples. T: tridymite; C: alpha-cristobalite; A: gamma-alumina.

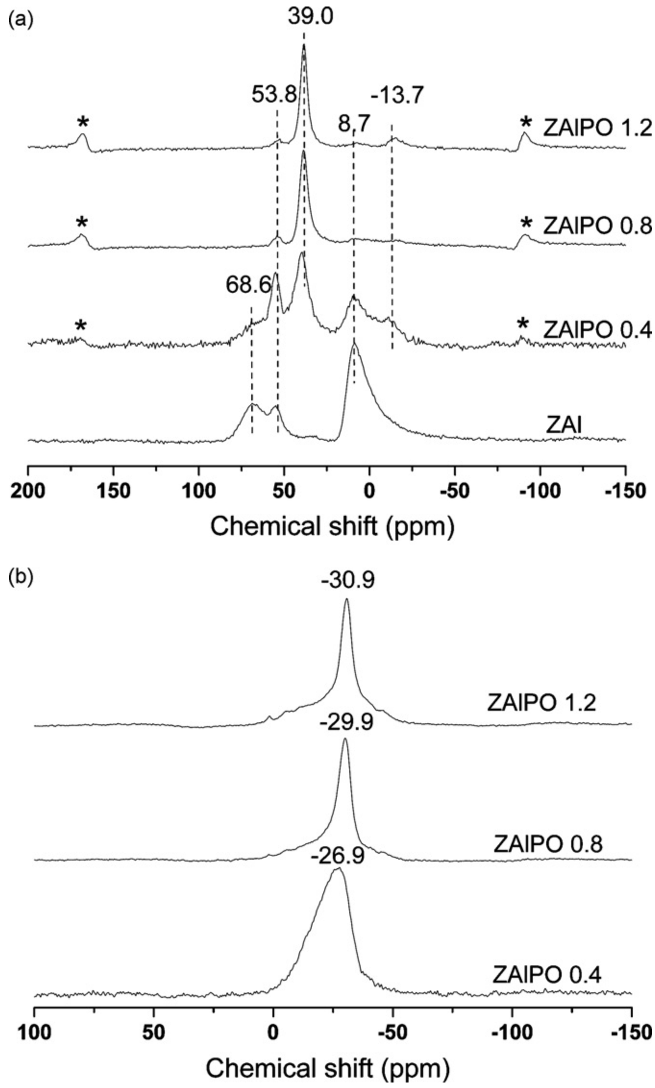

Fig. 2. (a) ^{27}Al and (b) ^{31}P MAS NMR spectra of the samples.

Nitrogen adsorption–desorption isotherms of the samples also indicate the changes in the textural properties of the binder by P addition (Fig. 3(a)). The pseudo-boehmite (Al) exhibits type IV adsorption isotherm with H1 hysteresis loop, as defined by IUPAC [25]. A loop at about $P/P^0 = 0.5–1.0$ representing the presence of a considerable amount of mesopores created by inter-crystalline voids of the alumina crystallites is observed in this sample. The shape of hysteresis loop indicates the presence of ink-bottle type pores. But, the pseudo-boehmite that includes some phosphorus (AlPO 0.8) exhibits very negligible amounts of mesopores. That means the addition of P to the alumina binder has completely removed the mesopore structure of the material. Since the inter-crystalline voids are the origin of mesoporosity in the pseudo-boehmite binder, the decrease in mesoporosity by P addition suggests a change in morphology of the alumina crystals in the binder. This can be explained by the effective interaction of P with the pseudo-boehmite to modify its structure and inter-crystalline voids. The addition of P to the pseudo-boehmite facilitates the chemical interaction between P and aluminum, and the interaction causes the change in morphology of the alumina crystallites to form amorphous aluminophosphate gel with no specific crystalline structure and hence no inter-crystalline voids. The resultant amorphous material yields a dense phase of AlPO up on calcination. As shown in Fig. 1, the X-ray diffraction patterns of AlPO binder

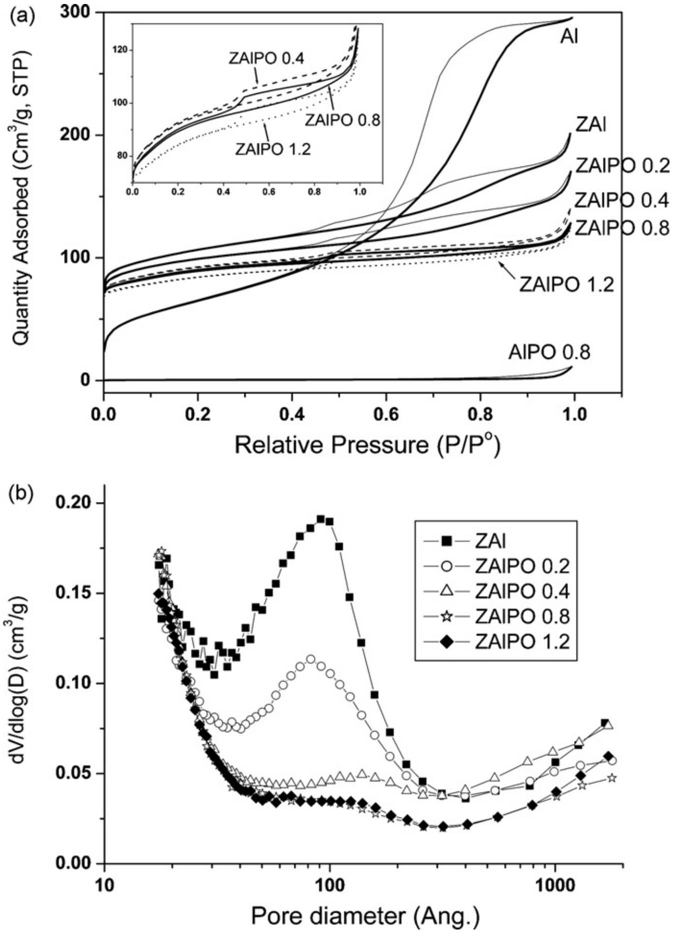

Fig. 3. (a) Nitrogen adsorption–desorption isotherm and (b) pore size distribution of the samples measured by BJH method.

indeed exhibit the peaks correspond to dense phase of alpha-cristobalite and tridymite. This observation supports the phase transformation of less-dense pseudo-boehmite into more-dense AlPO binder phase upon P addition that is responsible for the considerable decrease in mesoporosity of the binder. A significant decrease in surface area (from 236 to 1.9 $m^2\ g^{-1}$) of the alumina after the P addition also supports the formation of high-density AlPO.

The phenomenon of P-induced transformation of pseudo-boehmite into amorphous phase of aluminophosphate (and its conversion to high-density AlPO phase upon calcination) is expected to improve the mixing properties of the binder with zeolite. Moreover, the decrease of large pores in the binder is also known to improve the mechanical strength of the extrudates; such improvement is highly desirable for commercial applications [26,27]. Hence the extrudates are thoroughly studied for their physico-chemical properties and catalytic activity in MTP reaction.

3.2. Properties of AlPO bound ZSM-5 extrudates

In order to understand the role of phosphorus, we prepared various ZSM-5-based extrudates by varying the P amount in the pseudo-boehmite binder. The molar composition of binder is varied from P/Al = 0 (P-free pseudo-boehmite) to P/Al = 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 (P-containing pseudo-boehmite samples). During preparation of the binder-mixed-ZSM-5 extrudates, the percent of binder is always kept constant at 20 wt%. The resultant extrudates are characterized to understand the effect of P addition to the binder on the overall properties of the extrudates.

X-ray diffraction patterns of the samples given in Fig. 1 indicate that all the samples possess ZSM-5 structure. No distinguishable change is observed in the intensities of the samples with the addition of the binder or with the variation in composition of the binder. However, the samples show different adsorption isotherms (Fig. 3(a)). The extrudates prepared by mixing 20 wt% of pseudo-boehmite in the ZSM-5 (ZAl) exhibits the isotherm similar to that of the pure binder (Al), while the isotherms of P-containing extrudates (ZAlPO) show a reduction in the capillary condensation in mesopores. With increasing P content in the binder, the

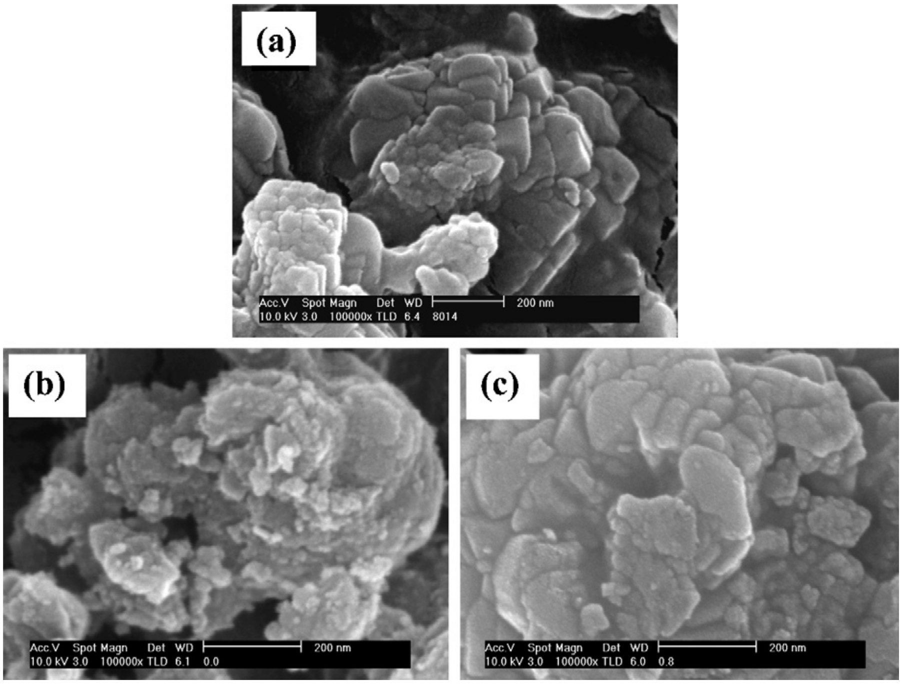

Fig. 4. SEM images of (a) ZSM-5, (b) ZAl and (c) ZAlPO 0.8 samples.

Table 1
Physico-chemical properties and coke analysis of extruded ZSM-5 catalysts.

Sample	Composition of binder[a]	Nitrogen adsorption			NH_3-TPD acidity (mmol g^{-1})			TGA results	
		BET surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Micropore volume ($cm^3\,g^{-1}$)	Weak (100–325 °C)	Strong (325–580 °C	Total	Reaction time (h)	Coke (wt%)
ZAl	$Al_{0.293}P_0O_x$	392.4	0.311	0.092	0.291	0.232	0.523	80	27.3
ZAlPO 0.2	$Al_{0.229}P_{0.046}O_x$	368.9	0.263	0.095	0.309	0.219	0.528	–	–
ZAlPO 0.4	$Al_{0.188}P_{0.075}O_x$	349.4	0.236	0.091	0.318	0.215	0.533	80	18.1
ZAlPO 0.6	$Al_{0.160}P_{0.096}O_x$	340.1	0.216	0.091	0.311	0.162	0.473	150	20.0
ZAlPO 0.8	$Al_{0.139}P_{0.111}O_x$	328.9	0.198	0.086	0.286	0.112	0.398	150	15.6
ZAlPO 1.0	$Al_{0.123}P_{0.123}O_x$	325.0	0.195	0.085	0.275	0.069	0.344	150	9.9
ZAlPO 1.2	$Al_{0.110}P_{0.132}O_x$	314.5	0.193	0.082	0.269	0.025	0.294	100	5.2
Al	AlOOH only	236.1	0.457	0					
AlPO 0.8	AlPO only	1.9	0.017	0					

[a] All the bound catalysts contain a ZSM-5 of $Al_{0.022}Si_{1.0}O_y$ composition.

extrudates exhibit decreases in mesoporosity. Above the value of P/Al = 0.6, mesopores in the sample have almost disappeared and the sample does not exhibit any loop representing the mesoporosity. The aspect of mesopore decrease is further appreciated from the pore diameter measurements (BJH method) of samples shown in Fig. 3(b). The trends in pore diameter of the P-loaded samples clearly reveal the systematic decrease in pore volume specifically at the pore diameter range of 50–300 Å related to the mesopores. Overall, the alumina binder (Al) as well as alumina bound ZSM-5 extrudates (ZAl) exhibit prominent mesoporosity, while the mesoporosity decreases with phosphorus addition in ZAlPO samples. The phenomenon of mesopore reduction in extrudates can be attributed to the role of P in converting the pseudo-boehmite crystals into amorphous alumina phase having no inter-crystalline voids responsible for mesoporosity. This is also reflected in the SEM images of the samples. The SEM images of the pure ZSM-5 zeolite and two binder-mixed-ZSM-5 extrudates with P/Al = 0 (ZAl) and 0.8 (ZAlPO 0.8) are shown in Fig. 4. The ZAl sample exhibits the presence of small granular phases of alumina on the zeolite crystals. But the ZAlPO 0.8 shows a clean morphology of zeolite. This may be due to the uniform distribution of fine amorphous particles of AlPO on the ZSM-5 crystals in the latter sample. This means that the interaction of P is responsible for the change in morphology of the alumina binder.

Textural properties of the samples prepared by P-containing alumina (AlPO binders) are given in Table 1. The phosphorus free sample (ZAl) exhibits higher surface area and pore volume. With the addition of phosphorus to the binder, the resultant ZAlPO extrudates exhibit a decrease in surface area from 392 to 314 $m^2\,g^{-1}$ and a decrease in total pore volume from 0.311 to 0.193 $cm^3\,g^{-1}$. This can be attributed to the formation of high-density AlPO by the interaction of phosphorus with the low-density alumina binder in the samples. Hence, the decreases in adsorption properties and surface area of the ZAlPO samples are due to the change in properties of the binder component, but are not due to the change in zeolite component. This aspect is further appreciated from the properties of the zeolite-free AlPO (AlPO 0.8) sample. The sample exhibits significant decrease in surface area and pore volume (Table 1). The pseudo-boehmite sample (Al) exhibits the surface area of 236 $m^2\,g^{-1}$ which is decreased to as low as 1.9 $m^2\,g^{-1}$ by P addition (AlPO 0.8). The micropore volume representing zeolitic pores is also slightly decreased from 0.092 to 0.082 $cm^3\,g^{-1}$. The major decreases in total pore volume and mesoporosity of the extrudates with marginal decreases in micropore volume and surface area clearly indicate that the added P has a major influence on the binder properties but not on the zeolite properties. However, the slight decrease in micropore volume observed in ZAlPO samples may be due to the increased inclusion of amorphous binder alumina inside the porous structure of zeolite with the increase of P amount in the binder. Such a close interaction between binder and zeolite will provide significant enhancement in the mechanical strength of extrudates. The mechanical strength of the extrudates is indeed increased from 3.1 MPa of ZAl to 8.2 MPa of ZAlPO 0.8, by the addition of P to the alumina binder. The intrusion of P-containing amorphous binder was also observed to alter the acidic properties of ZSM-5. At P/Al of 1.2 (ZAlPO 1.2), the sample exhibited 20% decrease in surface area and 40% decrease in pore volume when compared to ZAl sample.

The ammonia TPD plots of the calcined samples (Fig. 5(a)) exhibit a two-peak pattern: a low temperature peak at ~200 °C and a high temperature peak at ~450 °C. The former originates from the weakly acidic silanol groups that cover the external surface of

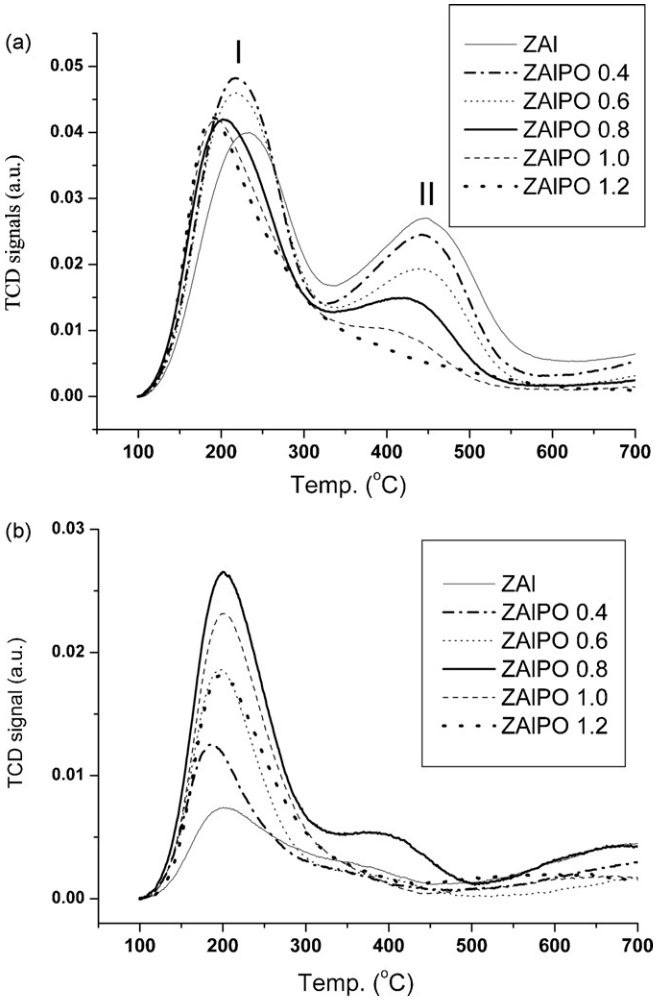

Fig. 5. NH_3-TPD of extrudates: (a) before hydrothermal treatment and (b) after hydrothermal treatment at 700 °C for 5 h under 100% steam.

Table 2
Product distribution at 10 h reaction time in methanol conversion over extruded ZSM-5 catalysts.

Sample	ZAl	ZAlPO 0.4	ZAlPO 0.6	ZAlPO 0.8	ZAlPO 1.0	ZAlPO 1.2
MeOH/DME conversion	100	100	100	100	100	98.1
Hydrocarbon distribution (yield, C-mol%)						
(I) C_1	4.6	1.3	0.7	0.4	0.3	0.35
(II) $C_2^=$–$C_4^=$ (C_2–C_4 paraffins)	72.6(11.3)	77.3(5.7)	82.9(2.6)	84.9(2.05)	83.3(1.2)	74.1(0.47)
$C_2^=$ (C_2^-)	20.8(0.3)	16.9(0.16)	14.7(0.09)	12.6(0.06)	8.1(0.03)	4.0(0.02)
$C_3^=$ (C_3^-)	37.0(3.2)	41.5(2.5)	46.9(1.25)	48.6(0.8)	51.1(0.3)	43.9(0.1)
$C_4^=$ (C_4^-)	14.8(7.6)	18.9(3.0)	21.7(1.3)	23.6(1.1)	24.0(0.7)	26.0(0.44)
$C_3^=/C_3^-$	11.4	16.5	37.7	55.0	156.4	439.0
$C_3^=/C_2^=$	1.7	2.5	3.2	3.8	6.2	10.8
(III) C_{5+}	11.3	15.7	13.8	12.5	15.1	23.1

the crystals and from lattice defects, while the latter peak arises from the Bronsted acid sites related with the framework aluminum of the ZSM-5. The strong and weak acidity of the samples are quantified based on the millimoles of ammonia desorbed at higher and lower temperatures, respectively (Table 1). All the samples exhibit the two-peak pattern but the intensity of high temperature peak representing strong acidity decreases with the increase of P in the binder. This observation clearly emphasizes the effective interaction of P with the binder and zeolite aluminum.

The P in the binder seems to interact with the Al–OH$^+$–Si groups of the zeolite and reduces the strong acidity; the phenomenon progresses with the P loading. This point can be clearly assessed from the data given in Table 1, where the strong acidity of the extrudates slightly decreased up to the P loading of P/Al = 0.4, whereas a drastic decrease in acidity is observed at higher P loadings (P/Al = 0.6–1.2). The strong acidity is decreased but the weak acidity is almost constant at all the levels of P loading. This observation suggests the effective interaction of the P in the binder with the framework aluminum (Bronsted acid sites) of the ZSM-5. Thus the AlPO based ZSM-5 sample with low acidity is expected to exhibit improved catalytic properties in terms of propylene yield, hydrothermal stability and coke resistance in MTP reaction.

3.3. *Catalyst performance in methanol to propylene (MTP) reaction*

The well-known mechanism for methanol conversion consists of the consecutive reaction steps of methanol dehydration to form DME; the resultant equilibrium mixture of methanol and DME undergoes further dehydration to produce light olefins, oligomers, paraffins and aromatics. The P modified binder in the catalyst is expected to control the strong acidity responsible for the formation of oligomers through the control of reaction at olefin formation stage. Performance of various catalysts in MTP reaction was studied and the product obtained after 10 h reaction time over these catalysts is given in Table 2. The product obtained is classified into C_1, light olefins ($C_2^=$–$C_4^=$) and C_{5+} hydrocarbons. Emphasis is given to maximize the formation of C_2–C_4 olefins with special reference to propylene. All the catalysts exhibited near 100% conversion of methanol, but the product yields are changed. With increasing P amount in the binder, the following changes are observed in the product yields:

1. C_1 and $C_2^=$ continuously decreased.
2. $C_3^=$ increased up to P/Al = 1.0 and then decreased at higher P loadings.
3. $C_4^=$ continuously increased.
4. The $C_2^=$–$C_4^=$ yields increased up to P/Al of 0.8 and then decreased above the value of 1.2.
5. Both $C_3^=/C_3$ and $C_3^=/C_2$ ratios have increased with the P loading.

These observations suggest the positive role of P in the binder for improved selectivity of C_2–C_4 olefins, especially $C_3^=$. Continuous increase of the $C_3^=/C_3$ ratio reveals the significant increase in the olefinicity of the C_3 hydrocarbon product with P loading. The difference observed in the yields of $C_3^=$ and $C_2^=$ clearly support that the formation and consumption of individual olefins are governed at different rates of the reactions. Earlier studies indicated that higher Si/Al of zeolite is better for increasing the propylene yields [28,29]. As the acidity decreases with the increase of Si/Al ratio, the moderate acidity in high Si/Al samples is responsible for the improved formation of propylene. The improved propylene yields obtained in the present study can be ascribed to the decrease in acidity of ZSM-5 caused by its mixing with AlPO binder. The TPD data indeed supports the decrease in strong acidity of AlPO bound ZSM-5 extrudates.

The positive aspect of P for improving propylene yield is continued up to the P/Al of 1.0 (Table 2). However, above this value, P addition caused decreases in overall conversion and product yields of the catalyst. In order to understand the optimum amount of P needed for catalyst performance in methanol conversion, we studied all the P-containing catalysts for their long time performance. Fig. 6 shows that the conversion of methanol is comparable on all the catalysts at the initial time of reaction. But the performance is varied depending on the amount of P loaded in the binder alumina. The ZAl and ZAlPO 0.4 exhibited decrease in conversion after 25 and 50 h of reaction time, respectively. While the performance is improved with the increase of phosphorus loading up to ZAlPO 0.8, the catalyst performance is again decreased at higher phosphorus loadings i.e., ZAlPO 1.0 and ZAlPO

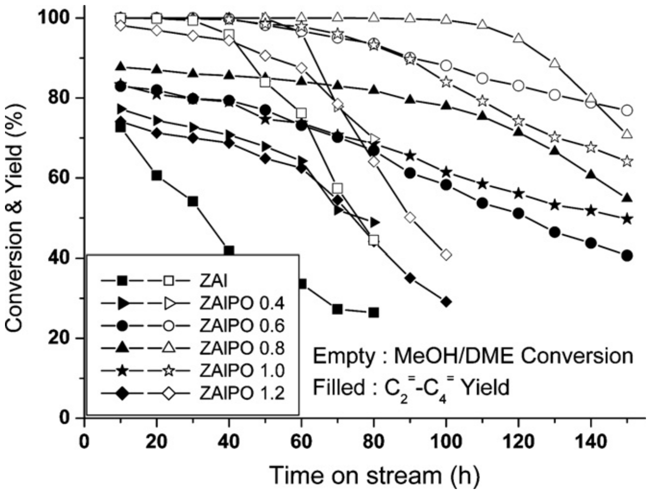

Fig. 6. Time-on-stream performances of catalysts in MTP reaction.

Table 3
Product distribution at 80 h reaction time in methanol conversion over extruded ZSM-5 catalysts.

Sample	ZAl	ZAlPO 0.4	ZAlPO 0.6	ZAlPO 0.8	ZAlPO 1.0	ZAlPO 1.2
MeOH/DME conversion	44.4	69.7	93.6	100	93.1	78.5
Hydrocarbon distribution (Yield, C-mol.%)						
(I) C_1	16.4	2.8	1.8	1.4	1.0	0.6
(II) $C_2^=$–$C_4^=$ (C_2–C_4, saturated)	26.4(0.45)	48.9(2.97)	66.8(5.7)	81.2(0.97)	68.5(0.94)	54.4(0.39)
$C_2^=$ (C_2^-)	1.2(0.2)	5.4(0.17)	10.4(0.1)	9.4(0.07)	4.3(0.04)	1.7(0.02)
$C_3^=$ (C_3^-)	1.3(0.05)	18.0(0.6)	37.9(0.7)	50.2(0.4)	37.8(0.1)	27.5(0.05)
$C_4^=$ (C_4^-)	23.8(0.2)	25.4(2.2)	18.4(4.9)	21.5(0.5)	26.3(0.8)	25.1(0.32)
$C_3^=/C_3^-$	24.5	29.8	48.6	123.3	275.5	550
$C_3^=/C_2^=$	1.0	3.3	3.6	5.3	8.6	15.6
(III) C_{5+}	0.9	15.0	19.1	16.2	22.5	23.0

1.2. The C_2–C_4 olefin yields shown in Fig. 6 also followed a similar trend with conversions. Among the various P-loaded catalysts, ZAlPO 0.8 exhibited the superior conversion and light olefin yields. The detailed product pattern obtained over this catalyst in methanol conversion is shown in Fig. 7. There is a slight increase in C_{5+} hydrocarbon yield, while a simultaneous decrease in ethylene is observed with reaction time on this catalyst. However, propylene yield is constant throughout the reaction time of 100 h. The results emphasize the exceptional improvement in reaction performance of the P-loaded catalyst. The improved performance of P-loaded catalyst may be due to the improvement in hydrothermal stability of the ZSM-5 facilitated by the interaction of P. Since, the presence of P in the binder decreased the acidity of the catalysts, the lower coke formation tendency of the resultant catalyst is also responsible for its long time stability in MTP reaction (Table 3).

3.4. Hydrothermal stability and coke resistance

The hydrothermal stability of the samples is studied by characterizing the structural and acidic properties of the catalysts after the treatment with water at high temperatures (700 °C) for 5 h. As shown in Fig. 5(b), all the samples exhibited decreases in acidity after the hydrothermal treatment (when compared to the untreated samples shown in Fig. 5(a)). Especially, the high temperature peak representing strong acidity is significantly decreased after the hydrothermal treatment of P-free (ZAl) sample. But the P-containing (ZAlPO) samples mostly lost strong acidity after the hydrothermal treatment with the exception to the ZAlPO 0.8 sample. However, the low temperature peak representing weak acid sites is in some extent protected in P-loaded samples and the amount of weak acidity remaining in the samples is increased with P loading i.e. from ZAlPO 0.4 to 1.2. The amount of weak acidity preserved after the treatment is also increased to some extent with the P loading. The ZAlPO 0.8 exhibited highest amount of stable acid sites after hydrothermal treatment. This may be due to the increased resistance of phosphorus-interacted aluminum sites in ZSM-5 against the dealumination. The X-ray diffraction patterns indicated no loss in crystallinity after the hydrothermal treatment.

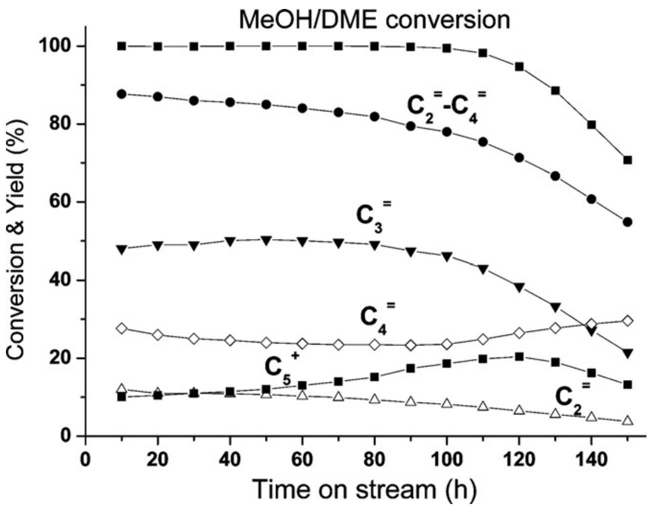

Fig. 7. Detailed product trends in MTP reaction over ZAlPO 0.8 catalyst.

The amount of coke formed on the catalysts after several hours of reaction was measured by TGA method. The P-free pseudo-boehmite containing catalyst (ZAl) exhibited a drastic decline in activity within 50 h of reaction time, whereas ZAlPO catalysts showed the reaction stability for 150 h. The amount of coke on the ZAl catalyst is also high even after 50 h reaction time. The data given in Table 1 indicates a decrease in formation of coke on the catalysts with increasing P amount. At the P loading of P/Al = 1.2 (ZAlPO 1.2), the catalyst exhibited the lowest amount of coke (~5 wt%). This is in accordance with the acidity values of the samples, where, the presence of P in the binder caused a decrease in strong acidity; hence, the amount of coke is also decreased on these catalysts.

4. Conclusions

Novel AlPO binders with amorphous phases are prepared by the treatment of pseudo-boehmite with phosphoric acid. The materials are identified as extremely suitable binders for the extrusion of ZSM-5 catalysts applied for methanol to propylene reaction. The advantage of the new amorphous binder lies in its effective interaction with the ZSM-5 to give extra-ordinary mechanical strength. Upon calcinations, the AlPO binder exhibits dense phases of alpha-cristobalite as major along with some tridymite phase. The undesired inherent properties of pseudo-boehmite, such as its self-catalytic activity and the possible interaction of aluminum in the binder with zeolite to form additional acid sites are nullified by the presence of phosphorus. In contrast to the conventional pseudo-boehmite, the AlPO binder exhibits no alumination and acidity increase to the zeolite. Rather, a decrease in strong acidity is observed in this catalyst due to the interaction of P with the zeolite. The acidity of the samples can be tailored through the optimization of the P loading in the binder to minimize side reactions of olefins to improve the propylene yield. At optimized P amount and reaction conditions, the catalyst Exhibits 50% yield to propylene at near 100% conversion of methanol.

Apart from the product yield, the presence of P in the binder also causes improved hydrothermal stability of the ZSM-5 catalyst and the improved coke resistance with time-on-stream. The catalyst exhibits improved stability in methanol conversion as well as light olefin yield in the studied period of 150 h.

Acknowledgements

The authors would like to acknowledge funding from the Korea Ministry of Knowledge Economy (MKE) through “Project of next-generation novel technology development” of ITEP. Dr. N. Viswanadham is thankful to Korea Federation of Science & Technology (KOSEF) for awarding a Brain-Pool fellowship.

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