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ORIGINAL PAPER

Vapour-phase condensation of methyl propionate with trioxane over alumina-supported potassium catalyst

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Alumina-supported potassium (K/Al_2O_3) catalysts using pseudo-boehmite as the precursor were prepared by the impregnation/calcination method, characterised by XRD, SEM, ICP, N_2 adsorption/desorption, CO_2-TPD methods and TG analysis, and applied to the vapour-phase condensation of methyl propionate with trioxane to produce methyl methacrylate. The results showed the catalysts' properties to be mainly affected by the calcined temperature (T_C) and the crystal structure. The sample calcined at 1100 °C exhibited the highest catalytic activity when mixed phases were formed and provided the appropriate specific surface area (S_{BET}) and surface basic properties. The effects of T_C, K-loading and reaction conditions on the catalytic performance were also investigated in a fixed-bed reactor. The yield of methyl methacrylate attained 29.2 % under the optimised conditions, and the deactivated catalyst could be completely regenerated by calcination.

Keywords: pseudo-boehmite, methyl methacrylate, potassium, calcined temperature, condensation

Introduction

Methyl methacrylate (MMA) is an important raw material for producing organic glasses. MMA is manufactured by several methods, the acetone/cyanohydrin (ACH) process being the principal one. However, extremely toxic and hazardous hydrogen cyanide (HCN) is entailed in the process, and a large amounts of co-produced ammonium sulphate and waste acid are produced. Although the ACH process has been improved, several reaction steps are involved (Nagai, 2001; Tai & Davis, 2007). Accordingly, many methods have been developed starting from diverse C2–C4 precursors, including propionaldehyde, methyl propionate (MP), isobutyric acid, propyne, isobutylene, etc. (Nagai, 2001; Wang et al., 2012). Among these, the MP route which consists of only two steps (Fig. 1), is attractive, since this process produces virtually no waste and the feedstocks can even be produced from coal and biomass (Hidai et al., 1987; Travalloni et al., 2008; Chang & Silvestri, 1977; Palekar et al., 1993).

Hence, much research has been devoted to the condensation reaction of MP with formaldehyde (FA) to produce MMA. Both acid and base catalysts are active in the reaction. Gogate et al. (1997) prepared a V–Si–P ternary catalyst for the aldol condensation reaction using propionate derivatives and formaldehyde as the starting materials, but the yield of MMA was low. Ai (2005) reported a silica-supported caesium hydroxide catalyst, and a 14.2 % conversion of MP was obtained with 85.9 % selectivity. An enhancement of the catalyst's performance was described by Li et al. (2013, 2014); this exhibited a 26.0 % conversion of propionic acid to MMA with 93.6 % selectivity on the catalyst Zr–Fe–Cs/SBA-15 using paraformaldehyde as the FA source.

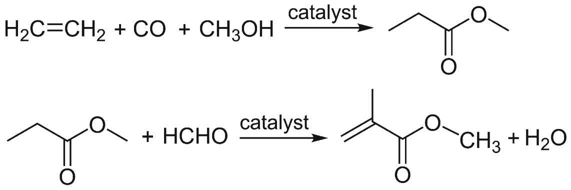

Fig. 1. Two-step reaction sequence for synthesis of MMA.

Aluminium oxide (alumina, Al_2O_3) is one of the most widely used materials employed as a catalyst

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*Corresponding author, e-mail: hemy_cczu@126.com or support (Amini et al., 2013; Stefanov et al., 2015; Kirszensztejn et al., 2009). A basic catalyst can generally be obtained by loading alkali metal or alkaline earth metal oxides onto Al_2O_3 (Maldonado et al., 2013; Sandesh et al., 2013; Isahak et al., 2012; Islam et al., 2013). However, the literature contains few reports on the synthesis of MMA over Al_2O_3-supported catalyst. Gaenzler et al. (1979) patented the K/Al_2O_3 catalyst for the condensation of MP and dimethoxymethane (methylal), and a 30.2 % conversion of MP was obtained with 60.1 % selectivity. Li et al. (2013) prepared Zr–Mg–Cs/γ-Al_2O_3 by impregnation and investigated the catalytic activity in the synthesis of MMA using polyformaldehyde as the source of FA. The conversion of MP and the selectivity of MMA attained 34.4 % and 62.2 %, respectively.

Al_2O_3 exists in a number of different phases, namely γ-, δ-, η-, θ- and α-Al_2O_3. Each has a unique crystal structure and property, and the phase as the support has a significant effect on the catalytic activity. However, the literature contains no investigation of this in the condensation of MP and FA. Pseudo-boehmite, a low crystalline aluminium oxide hydroxide (AlOOH), is useful as a precursor for the preparation of catalyst supports and porous materials. The calcination of pseudo-boehmite at different temperatures can result in Al_2O_3 of various phases (Yang et al., 2013; Hong et al., 1997; Moroz et al., 2011).

In the present study, various K/Al_2O_3 catalysts were prepared by the impregnation/calcination method using pseudo-boehmite as the precursor. The catalysts so obtained were characterised and introduced into the vapour-phase condensation reaction of MP and FA in a continuous-flow fixed-bed reactor. The influence of T_C, K-loading, and reaction conditions (reaction temperature (T_R), MP content and MP/FA ratio) on the reaction were investigated. The stability and reproducibility of the K/Al_2O_3 catalyst were also studied.

Experimental

Preparation and characterisation of catalysts

Methyl propionate ($\geq$ 99.0 %), trioxane (1,3,5-trioxane, $\geq$ 99.0 %) and potassium hydroxide (KOH) ($\geq$ 99.0 %) were obtained from Aladdin (China). Pseudo-boehmite (industrial grade; Al_2O_3 mass content: 70.19 %, analysed by thermogravimetric (TG) analysis; Dai Qi Engineering Technology, China).

K/Al_2O_3 catalysts with different K-loading were prepared by the wetness impregnation/calcination method using pseudo-boehmite as the precursor. A solution of KOH of an appropriate concentration was added to the pseudo-boehmite carrier. The resulting mixture was impregnated for 6 h, dried overnight at 80 ℃ then calcined at different temperatures for 3 h. For comparison, a K/γ-Al_2O_3 catalyst with 3.01 % of K-loading was also prepared by the wetness impregnation of γ-Al_2O_3 (99.99 %, 10 nm, $r \leq 20$ nm, specific surface area (S_{BET}) ≤ 200 m^2 g^{-1}; Aladdin, China) following the same procedure.

Powder X-ray diffraction (XRD) patterns of the as-synthesised catalysts were analysed using a Rigaku D/max 2500 PC X-ray diffractometer (Rigaku, Japan) with CuK_α (1.5402 Å) radiation at 10 min^{-1}. A JEOL JSM-6360LA scanning electron microscope (Jeol, Japan) was used for the scanning electron microscopy (SEM) study. The S_{BET} of samples were determined by the BET method using a ASAP2010C apparatus (Micromeritics Instrument Corporation, USA), and the gas adsorbed at −196 ℃ was pure nitrogen. Temperature-programmed desorption (TPD) of CO_2 was performed on CHEMBET-3000 equipment (Quantachrome Instruments, USA). The samples were first calcined at 600 ℃ (450 ℃ for the sample calcined at 450 ℃) for 3 h and subsequently cooled to 100 ℃ under a helium flow (30 mL min^{-1}) and saturated with dry gaseous CO_2 (99.999 %, 50 mL min^{-1}) at 100 ℃ for 30 min. The samples were then purged with a helium flow (30 mL min^{-1}) for 30 min. The CO_2-TPD was performed at a rate of 10 ℃ min^{-1} to 550 ℃, and was maintained at 550 ℃ for 90 min (450 ℃ for the sample calcined at 450 ℃). TG curves were obtained using a Shimadzu DTG-60H analyser (Shimadzu, Japan). The samples were heated from ambient temperature to 1200 ℃ at a rate of 10 ℃ min^{-1} under a nitrogen flow of 30 mL min^{-1}. Inductively coupled plasma analysis (ICP; Varian Vista-AX, USA) was used to analyse the compositions of the samples.

Reaction procedure for condensation

The condensation of MP with FA was carried out in a continuous-flow fixed-bed reactor at atmospheric pressure. The reactor was made of a stainless steel tube (length: 60 cm; internal diameter: 10 mm) mounted vertically in the furnace. The catalyst (20 mL, approximately 21 g) was placed in the middle of the reactor. The reaction was performed at 320 ℃. In this study, the mixed reactant consisting of MP and trioxane with a MP/FA mole ratio of 1 : 2 dissolved in CH_3OH was fed into the reactor via an advection pump at a feed-rate of 0.3 mL min^{-1}. Nitrogen was introduced from the top of the reactor at a flow of 60 mL min^{-1}. The weight hourly space velocity (WHSV: g of feed flowing per g of catalyst per h) was approximately 1.6 h^{-1}. The effluent gases were cooled using a condensate trap. The samples were collected at intervals and analysed off-line by gas chromatography (Shimadzu GC-2010AF, Japan) using a Chromopak capillary column and FID detector. The identification of the products was further confirmed using GC-MS (Shimadzu GCMS-2010, Japan). The conversion of MP and selectivity of MMA presented here are

Table 1. Textural properties of catalysts using different precursors and T_C^a

Support	T_C/℃	S_{BET}/(m^2 g^{-1})	V_P/(cm^3 g^{-1})	AD_P/nm
Pseudo-boehmite[b]	–	353.3	0.32	3.6
Pseudo-boehmite	450	203.3	0.28	5.5
Pseudo-boehmite	650	205.0	0.35	6.9
Pseudo-boehmite	850	157.9	0.28	7.0
Pseudo-boehmite	1100	47.7	0.14	11.9
Pseudo-boehmite	1200	0.07	0.008	477.9
γ-Al_2O_3	850	120.2	0.49	16.5

a) K-loading: 3.06 %; *b*) no K-loading.

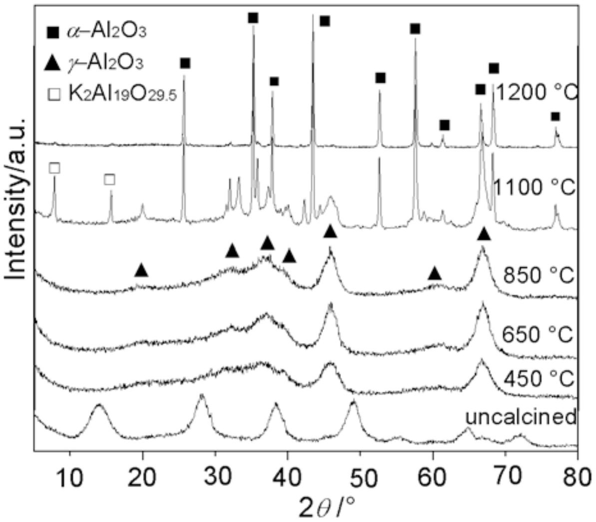

Fig. 2. XRD patterns of supported catalysts using pseudo-boehmite as precursor with different T_C.

based on the GC calculations using butyl alcohol as the internal standard reference compound.

Results and discussion

XRD analysis

For the pseudo-boehmite, the T_C has a significant effect on the structure of the samples. To investigate the effect of the different crystal structures on the catalytic activity, the samples were calcined from 450℃ to 1200℃ and their XRD patterns are shown in Fig. 2. The diagrams are vertically displaced and the same scale is used in order to easily compare the reflections of different samples. The γ phase was formed gradually as the temperature increased from 450℃ to 850℃; the patterns show common features with reflections located at the angles typical of a γ phase (Yang et al., 2013).

When the T_C increased to 1200℃, the α phase was gradually formed with reflections located at the angles typical of an α phase (Yang et al., 2013). In the calcination process, the pseudo-boehmites are first transformed into thermodynamically metastable transition aluminas, e.g., γ-, δ- and θ-Al_2O_3 in a topotactic way. The stable α phase formed from transition aluminas cannot be obtained below 1200℃ (Yang et al., 2013; Hong et al., 1997), involving a considerable structure rearrangement. The results can be verified by TG analysis. From the TG and DTA curves (Fig. S1), no mass loss occurs beyond approximately 480℃, while at least two exothermic peaks were observed, at 481.3℃ and 992.5℃, respectively. These are further indications that the stable α phase was forming under calcination.

Several phases were formed when the T_C was set at 1100℃. Two new 2θ diffraction peaks appeared at 7.8° and 15.6°, respectively, corresponding to the hexagonal crystals of $K_2Al_{19}O_{29.5}$ (JCPDS 44-1009). Therefore, the sample calcined at 1100℃ consisted of γ-, α-Al_2O_3 and $K_2Al_{19}O_{29.5}$.

Textural properties analysis

The supported potassium catalysts using pseudo-boehmites as the precursor calcined at different T_C were also examined using the nitrogen adsorption/desorption method. The values of the S_{BET}, pore volume (V_P) and pore size (average pore diameter, AD_P) of these samples are summarised in Table 1. A decrease in the S_{BET} from 203.3 m^2 g^{-1} to approximately 0.07 m^2 g^{-1} and a decrease in V_P from 0.28 m^3 g^{-1} to about 0.008 m^3 g^{-1} were observed upon increasing the T_C from 450℃ to 1200℃, which may be attributed to the different crystal structures formed at different T_C. Such a calcination process at such a high temperature should result in α-Al_2O_3 particle growth, generally along with serious sintering, particle coarsening and agglomeration, forming a large vermicular substructure. As a result, the AD_P increased slightly at below 1100℃, and rapidly, to 477.9 nm, at 1200℃.

SEM analysis

The images of the unloaded and the loaded Al_2O_3 samples with different T_C are shown in Fig. 3. Fig. 3D reveals that the as-synthesised parent pseudo-

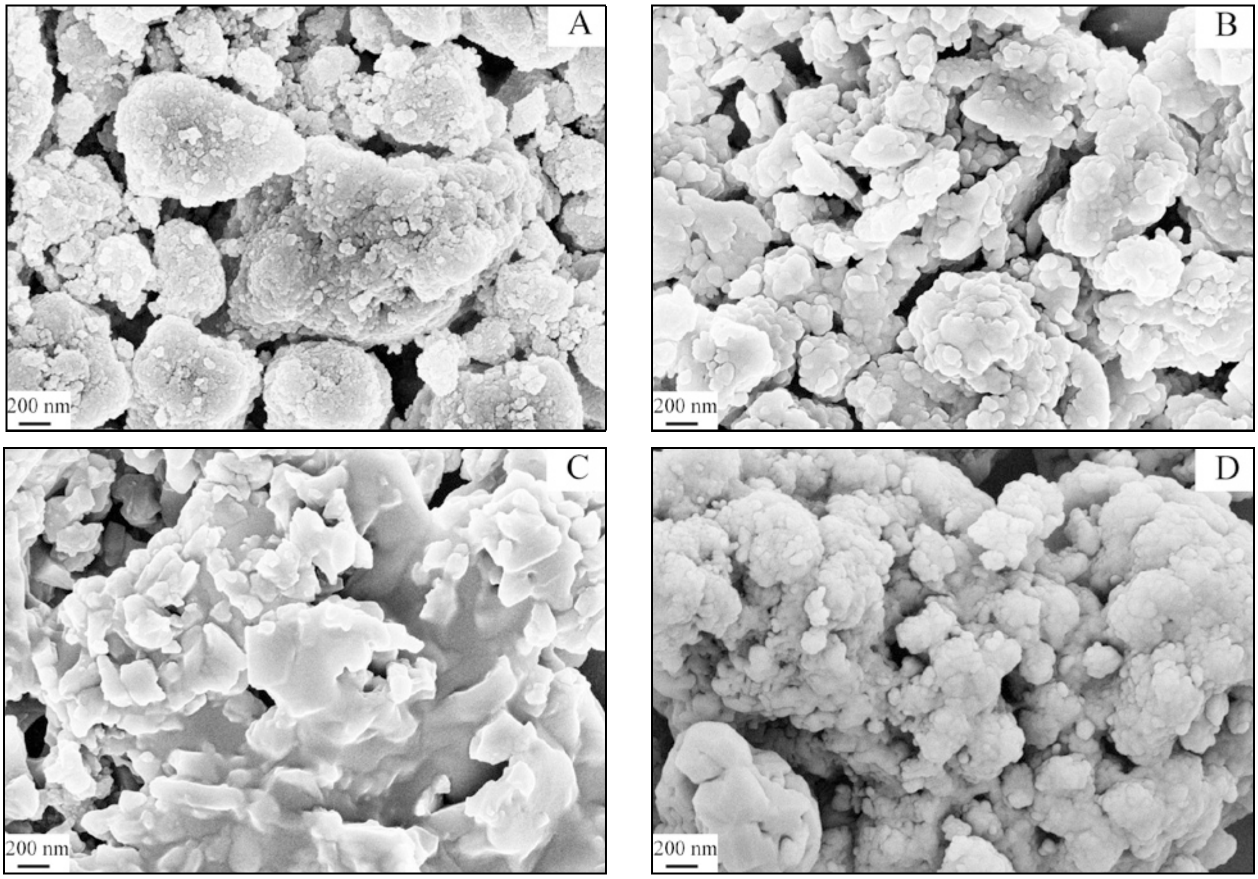

Fig. 3. SEM images of alumina-supported catalysts calcined at 850 °C (A), 1100 °C (B), 1200 °C (C) and blank sample (1100 °C) (D).

boehmite sample consisted of well-defined plate-like macro-structures aggregated with a relatively uniform size of 100 nm. After potassium incorporation, a slight aggregation in the macroscopic structure occurred, but the plate-like domains with average sizes of 200 nm were maintained (Figs. 3A and 3B) when the T_C was below 1200 °C. However, when the T_C increased to 1200 °C, the particles significantly aggregated (Fig. 3C), further revealing the changes in textural properties.

Basicity analysis

The analysis of base sites on the surfaces of the prepared samples was determined by step-wise TPD of CO_2. The analysis results given in Fig. 4 indicate that the basic strength and amount of the prepared samples were significantly affected by the T_C, as well as the crystal structures of Al_2O_3. There were mainly two desorption ranges for all the samples. One peak was centred at around 150 °C and assigned to the weak basic sites. The second peak is assigned to the moderate basic sites between 250 °C and 300 °C. From the curves, it can be observed that the number of weak basic sites decreased as the T_C increased, while the number of moderate basic sites was highest when the sample was calcined at 1100 °C, indicating that new moderate basic sites had formed on the surface. The sample calcined at 1200 °C had the lowest total base amount which could be attributed to the decreased S_{BET}. These results were verified by textural properties and SEM analysis. With regard to the XRD anal-

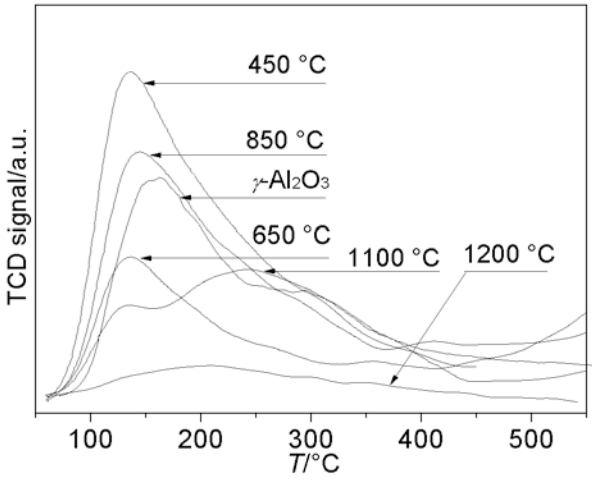

Fig. 4. CO_2-TPD profiles of alumina-supported catalysts calcined at different temperatures.

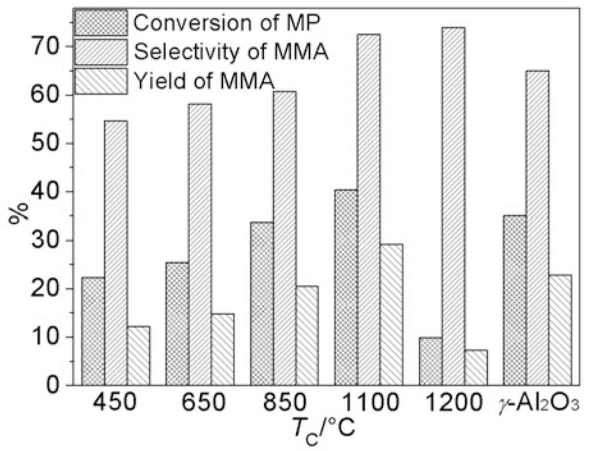

Fig. 5. Effect of T_C of alumina-supported catalysts on catalytic activity. Reaction conditions: K content: 3.06 %; T_R: 320 ℃; MP/FA ratio: 1 : 2; MP content in CH_3OH: 20 %; feed-rate: 0.3 mL min^{-1}; nitrogen flow: 60 mL min^{-1}.

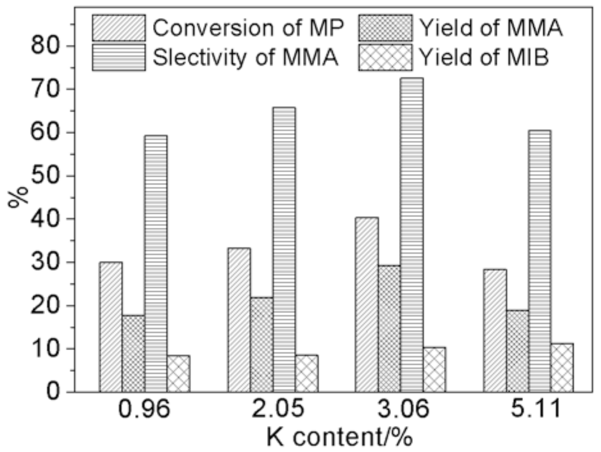

Fig. 6. Effect of K content of alumina-supported catalysts on catalytic activity. Reaction conditions: T_C: 1100 ℃; T_R: 320 ℃; MP/FA ratio: 1 : 2; MP content in CH_3OH: 20 %; feed-rate: 0.3 mL min^{-1}; nitrogen flow: 60 mL min^{-1}.

ysis, the moderate basic sites might have resulted from the new phase, i.e. hexagonal crystals of $K_2Al_{19}O_{29.5}$.

Catalytic performance of catalysts for condensation of MP with FA

As the source of FA, formalin (an aqueous solution of FA) is a recognised and convenient compound. However, the reaction is markedly hindered by the water vapour present in the feed (Ai, 2005). Therefore, methylal and trioxane ($(HCHO)_3$) have been claimed as effective (Ai, 1990a, 1990b; Albanesi & Moggi, 1983; Ai et al., 2003), which can be decomposed under the reaction conditions. Although methylal is decomposed even at a short contact time of 0.6 s (Ai, 1990b), the formation of methanol may influence the selectivity of the reaction. Therefore, trioxane (calculated as three molecules of FA) was selected as the source of FA in the present study.

Effect of T_C

For the supported potassium material using pseudo-boehmites as the precursor, the T_C has a significant effect on the crystal structure of the samples and their surface properties. The catalytic activities of the samples calcined at different temperatures are illustrated in Fig. 5. The yield of MMA increased gradually as the T_C increased from 450 ℃ to 1100 ℃, while the lowest conversion was obtained for the sample calcined at 1200 ℃. The results indicate that the S_{BET} and the base properties of the catalysts play an important role in the condensation, and the activities of these catalysts increase as the number of moderate basic sites increases.

To elucidate the effect of the crystal structure of Al_2O_3 on the catalytic activity, γ-Al_2O_3-supported potassium was also prepared using the impregnation method. The sample was calcined at 850 ℃ to retain the γ phase. Fig. 5 shows that the pure γ-Al_2O_3-supported potassium did not exhibit the best yield, further indicating that the high catalytic activity of K/Al_2O_3 is related to the formation of a new phase and surface basic property of the catalyst (Fig. 4).

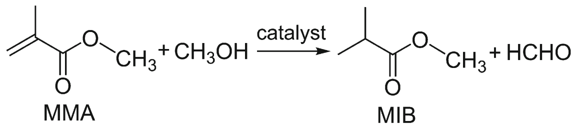

Fig. 7. Formation of main by-product MIB from MMA using K/Al_2O_3 catalysts.

Effect of potassium content

The results of the condensation reaction over K/Al_2O_3 catalysts with different K contents are summarised in Fig. 6. It is clear that the K content exerts a significant effect on the catalytic performance. The MP conversion markedly increased with an increase in K content, while the selectivity of MMA decreased when the K content attained 5.11 %. On the other hand, the yield of the main by-product, methyl isobutyrate (methyl 2-methylpropanoate; MIB) (Fig. 7), increased gradually, which should be the reason for the decrease in the selectivity of MMA.

The CO_2-TPD analysis (Fig. 8) shows that, as the K-loading increased, the number of weak basic sites decreased. However, the number of moderate basic sites increased when the content was in the range of 0.96–3.06 % and reached the lowest value when the K content was 5.11 %, which may be due to the

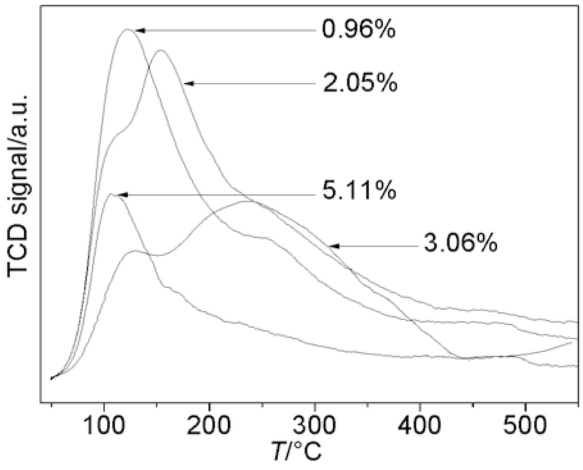

Fig. 8. CO_2-TPD profiles of K/Al_2O_3 catalysts with different K-loading.

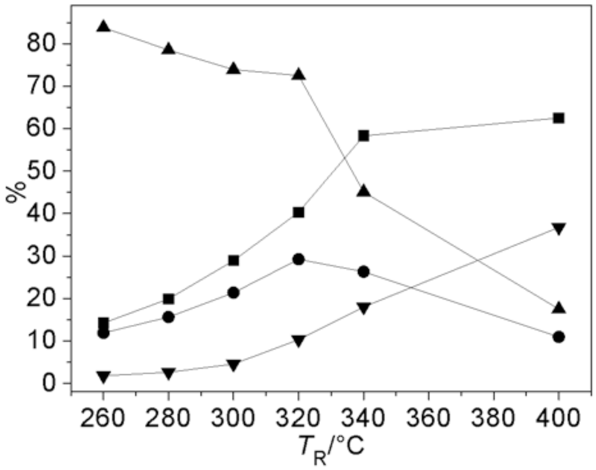

Fig. 9. Effect of T_R on condensation reaction: conversion of MP (■); yield of MMA (●); selectivity of MMA (▲); yield of MIB (▼). Reaction conditions: K content: 3.06 %; T_C: 1100 °C; MP/FA ratio: 1 : 2; MP content in CH_3OH: 20 %; feed-rate: 0.3 mL min^{-1}; nitrogen flow: 60 mL min^{-1}.

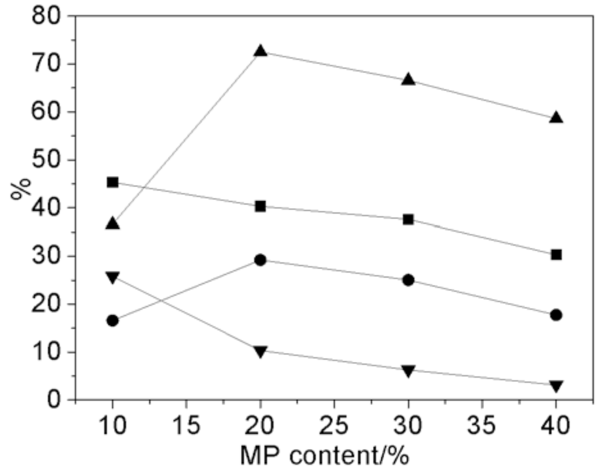

Fig. 10. Effect of MP content on condensation reaction: conversion of MP (■); selectivity of MMA (▲); yield of MMA (●); yield of MIB (▼). Reaction conditions: K content: 3.06 %; T_C: 1100 °C; T_R: 320 °C; MP/FA ratio: 1 : 2; feed-rate: 0.3 mL min^{-1}; nitrogen flow: 60 mL min^{-1}.

formation of $K_2Al_{19}O_{29.5}$ as the major phase. This phenomenon can also be verified by the XRD patterns. The diffractograms of the catalyst with different amounts of K supported on pseudo-boehmite calcined at 1100 ℃ are shown in Fig. S2. It may be noted that weak signals ($2\theta = 7.8°$ and $15.6°$) were observed when the K content was below 2 % and the signals increased as the K content increased, indicating that higher amount of supported K favoured the formation of the hexagonal crystals of $K_2Al_{19}O_{29.5}$. When the K content increased to 5.11 %, $K_2Al_{19}O_{29.5}$ became the major phase, indicating that the phase transition temperature may also be influenced by the K content. From the above results and analysis, it may be concluded that the catalytic activity of K/Al_2O_3 in condensation may be related to the moderate basic sites and its amount.

Effect of reaction temperature

To elucidate the effect of T_R on the condensation reaction, the reaction was performed from 260 ℃ to 400 ℃, with the results shown in Fig. 9. The conversion of MP increased rapidly with the T_R increase, while the selectivity towards MMA decreased sharply when the temperature was higher than 340 ℃. The highest yield of MMA was obtained at T_R of 320 ℃ under the reaction conditions selected. Fig. 9 clearly shows that MIB is prone to be formed at higher T_R, which can explain the trend of the selectivity of MMA.

Effect of MP content

In the present study, methanol was used as the solvent to avoid the hydrolysis of MP and MMA, and no acid was detected in the products. However, a reaction between MMA and methanol can result in the main by-product MIB, which decreases the selectivity of the reaction. Hence, the effect of the MP content on the reaction was investigated and the results are shown in Fig. 10. As the MP content increased, the selectivity and yield of the MIB decreased, which favoured the production of MMA. However, the conversion of MP gradually decreased when the MP content further increased, which could be interpreted by “Le Châtelier’s principle”.

Effect of MP/FA ratio

The results of the condensation reaction for four

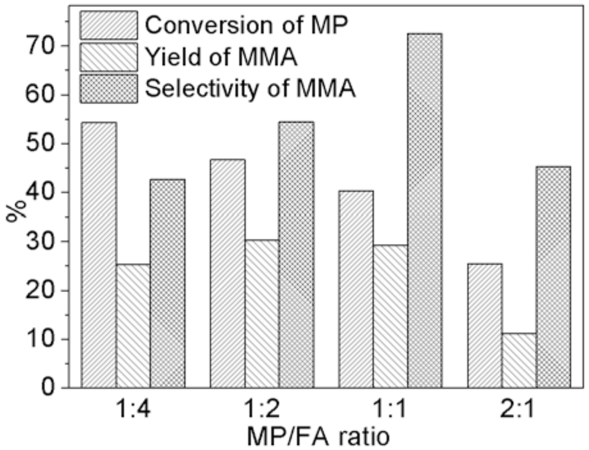

Fig. 11. Effect of MP/FA ratio on condensation reaction. Reaction conditions: K content: 3.06 %; T_C: 1100 ℃; T_R: 320 ℃; MP content in CH_3OH: 20 %; feed-rate: 0.3 mL min^{-1}; nitrogen flow: 60 mL min^{-1}.

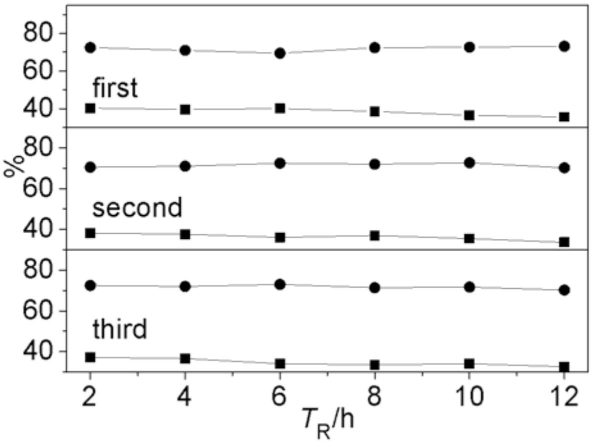

Fig. 12. Catalytic activity of regenerated catalyst: conversion of MP (■); selectivity of MMA (●). Reaction conditions: K content: 3.06 %; T_C: 1100 ℃; T_R: 320 ℃; MP/FA ratio: 1 : 2; MP content in CH_3OH: 20 %; feed-rate: 0.3 mL min^{-1}; nitrogen flow: 60 mL min^{-1}.

different MP/FA mole ratios are shown in Fig. 11. As the MP/FA ratio increased, the conversion of MP decreased whereas the selectivity of MMA increased. However, the selectivity decreased to 46 % when the MP/FA mole ratio increased to 2 : 1. The best results were obtained when the MP/FA mole ratio was 1 : 1. Under the conditions selected, the conversion of MP achieved 40.3 % with a moderate selectivity of 72.5 %.

Catalyst stability and reproducibility

The stability and reproducibility of the K/Al_2O_3 catalyst were also investigated. Under the optimal conditions, the reaction performed continuously for 12 h, and the conversion of MP decreased slightly, whereas the selectivity of MMA remained at approximately 70 %. Then the K/Al_2O_3 catalyst was regenerated simply by calcination under an air flow at 450 ℃ for 4 h in the fixed-bed reactor. Fig. 12 shows that the catalytic activity of the regenerated catalyst was almost the same as that of the fresh catalyst, indicating that the K/Al_2O_3 catalyst had excellent reproducibility in the activity. After the reaction, the K content of the used K/Al_2O_3 catalyst was analysed by ICP and the results revealed that the K content changed from 3.06 % to 2.98 %. There was almost no leaching of the K ion after the catalytic reaction. The XRD pattern of the recycled K/Al_2O_3 catalyst in Fig. S3 shows that the structure of the catalyst was not changed in the catalytic condensation.

Conclusions

In the present study, alumina using pseudo-boehmites as the precursor of supported potassium catalysts were prepared by the impregnation/calcination method, characterised and applied to the production of MMA from MP and trioxane in a fixed-bed reactor. The results indicated that the T_C had a significant effect on the structure and properties of the catalyst. As the T_C increased from 450 ℃ to 1200 ℃, the crystal structure of Al_2O_3 gradually changed and finally formed the α-phase. The highest yield of MMA was obtained at the T_C of 1100 ℃, when mixed phases were formed and provided the appropriate S_{BET} and superficial basic properties. In addition, the effects of the K content and reaction conditions (T_R, MP content and the MP/FA ratio) on the catalytic performance were also investigated. Under the optimal conditions, the conversion of MP and the selectivity of MMA attained 40.3 % and 72.5 %, respectively. The catalyst can be regenerated simply by calcination under an air flow at 450 ℃ in the reactor without any obvious decrease in catalytic activity. In comparison with the γ-Al_2O_3-supported catalyst, pseudo-boehmite is more economical and convenient, and exhibits similar catalytic properties, suggesting that, from the commercial perspective, the K/Al_2O_3 catalyst can be produced on an industrial scale.

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Supplementary data

Supplementary data associated with this article can be found in the online version of this paper (DOI: 10.1515/chempap-2016-0076).

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