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Studies of Al_2O_3–K catalysts prepared using various precursors for diesel soot elimination

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Abstract

The optimal calcination temperature was 600 °C and the highest activities were obtained at Al:K molar ratios of 3:1, 1:1 and 1:1 for Al_2O_3/KNO_3, $Al(NO_3)_3/KNO_3$ and Al_2O_3/KOH precursor combinations, respectively. The active compound in the catalyst prepared by $Al(NO_3)_3/KNO_3$ was KNO_3 exclusively. However, the catalytic activity of the catalysts prepared by Al_2O_3/KOH was affected by the formation of $K_2Al_2O_4$ and K_2CO_3 compounds. The catalysts prepared by all precursor combinations behaved a comparable thermal stability. High temperature aging of the catalysts would result in the loss of surface area and/or active compounds, and hence the deterioration of their catalytic activities.

Keywords: Al_2O_3; Potassium; Catalytic activity; Diesel soot elimination

1. Introduction

In order to remove the soot collected by diesel particulate filter (DPF) continuously, the usage of catalysts with a high soot oxidation activity at exhaust temperature of 175–400 °C is a more practical technique for DPF regeneration [1]. In past decades, many catalyst systems capable of oxidizing the soot at the exhaust temperature range have been reported. Among these catalysts, the alkali metal promoted catalysts such as K–Cu [2] and K–Co [3], Co–Ba–K [4], Cu–K–Mo [5], Cu–V–K [6], V–K [7,8], and Mg–K [9] were widely studied because the researchers believed that the formation of molten salts would assure a good contact between the catalyst and soot [10,11]. In addition to molten salts, the rare earth element based catalysts were also investigated for diesel soot combustion, such as Ce–La [12], La–Cr [13], Pr–Cr [14], La–K [15], La–K/Cr [16], La–K–Mn–O [17], La–K–Cu/V [18], Sm–K [19] and Co–Ce [20]. A study carried out by Miró et al. suggested that the good catalytic activity of CeO_2–K(KOH) catalyst is attributed to the redox property of CeO_2. Basically, this theory is related to the redox mechanism that introduces the carbon oxidation by lattice oxygen from the catalyst and re-oxidation of the catalyst by oxygen from the gas phase [21–25].

Past studies have also shown the important role of adding alkali metal salts or alkaline-earth metal salts into metal oxide catalyst systems for catalytic activity enhancement [26–29], but the intrinsic principle involved is not totally understood. Recently, the catalytic formation of intermediate carbonate species promoted by alkali metals during the oxidation process has been proposed to explain the enhancement effect of these alkali metals [30,31]. In our previous studies, it was found that CeO_2 showed a very weak catalytic activity of soot oxidation without addition of K element [32]. In this work, Al_2O_3–K catalysts prepared with various types of precursors were studied in terms of catalytic activity and thermal stability. The study results could also be used to evaluate the compatibility of the K-containing catalysts with Al_2O_3, a potential filter material.

2. Experimental materials and methods

2.1. Catalyst preparation and characterization

The chemicals used for catalyst preparation were of analytical grade KOH, KNO_3, $Al(NO_3)_3\cdot 6H_2O$ (Analytical purity, Shanghai Chemical Regents Co. Ltd., China) and α-Al_2O_3 powders (Average particle size 3 μm, purity 99.5%, Shandong Aluminum

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Co. Ltd., China). The catalyst precursors with the combinations of Al_2O_3/KNO_3, $Al(NO_3)_3/KNO_3$ and Al_2O_3/KOH at different Al:K atomic molar ratios (Al:K = 10:1, 3:1, 1:1, 1:3) were loaded onto porous alumina ceramics according to the procedures reported previously [8,19] followed by calcination in a furnace at 500, 600 and 700 °C for 3 h to obtain the final bulk ceramics supported catalysts. Some samples were also heat-treated at 600 °C for 48 h to determine their long-term thermal stabilities. KOH, KNO_3, $Al(NO_3)_3$ and α-Al_2O_3 were also ground into fine powders (about 3 μm) and pressed onto the ceramic substrate to test their catalytic activity. X-ray diffraction (Rigaku D/max-rA, Rigaku, Japan) was used to characterize the un-supported catalysts calcined in an alumina crucible. Scanning electron microscopy (SEM, Jeol-6700F, Japan) was used to determine the surface morphologies of the supported catalysts.

2.2. Catalytic activity characterization

A temperature-programmed reaction (TPR, homemade) system equipped with a non-disperse infrared CO and CO_2 analyzer (Wuhan Cubic Optoelectronics Co. Ltd., China) and data acquisition and recording units was used to characterize the catalytic activity of the prepared catalysts [8]. Before catalytic oxidation activity testing, the catalysts were allowed to contact with air for at least 24 h followed by TPR tests without soot coating to eliminate the absorbed CO_2. After testing, the catalysts were taken out from the furnace and coated with soot by fuming them above the burning diesel and the soot/catalyst contact is loose, similar to the contact condition produced from diesel exhaust [32]. The catalyst coated with soot (the catalyst mass was about 100 mg and the soot coated on the catalyst was about 10 mg) was cooled in the furnace with a N_2 atmosphere to the temperature below 100 °C. Then, the second TPR test was carried out at a heating rate of 10 °C/min with the CO_2-removed air fed into the reaction equipment at a flow rate of 1 L/min. The simultaneous CO_2 concentration detection of the outlet gas was carried out and the soot ignition onset temperature (IOT) where the CO_2 concentration started to increase was determined from the reaction curves.

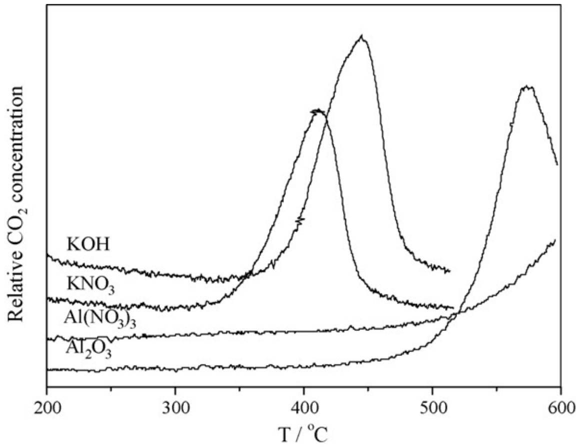

Fig. 1. TPR profiles (with soot coating) of individual compounds used for catalyst preparation.

3. Results and discussions

Because the amount of soot deposited on the catalysts will affect the CO_2 peak intensity and temperature during the oxidation process, the catalytic activities of catalysts were evaluated by IOT together with the peak temperature as a reference. The catalytic activities of individual compounds used for catalyst preparation were also studied and the resulting TPR profiles are shown in Fig. 1. It can be clearly seen from this figure that the soot began to be oxidized at about 450 and 480 °C on Al_2O_3 and $Al(NO_3)_3$ powders separately, suggesting their low catalytic activity of soot oxidation. KOH and KNO_3, however, displayed much lower IOTs of about 350 and 320 °C, respectively, indicating their high catalytic oxidation activity. The catalytic activities of the catalysts prepared with $Al(NO_3)_3/KNO_3$, Al_2O_3/KNO_3 and Al_2O_3/KOH combinations were measured by TPR in terms

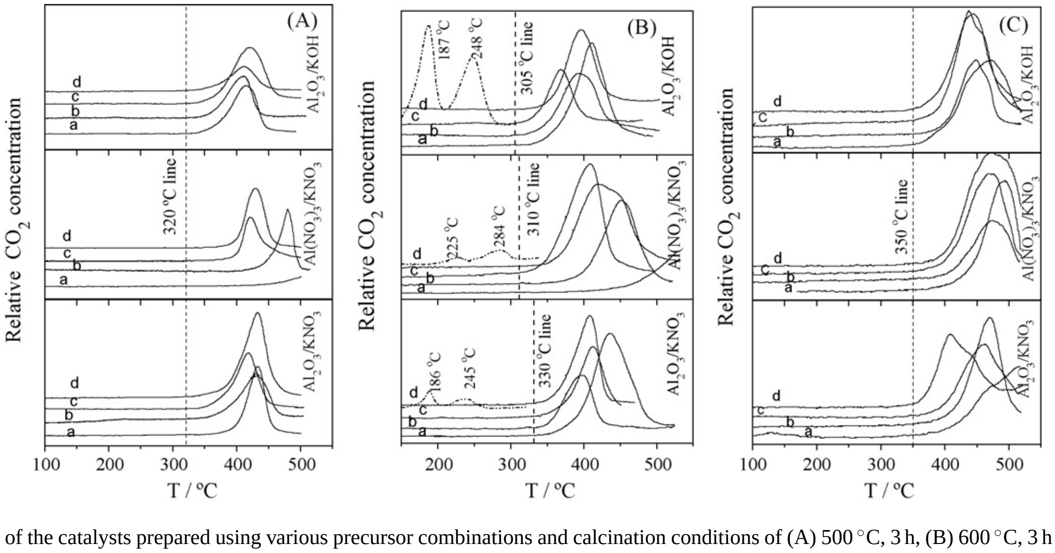

Fig. 2. TPR profiles of the catalysts prepared using various precursor combinations and calcination conditions of (A) 500 °C, 3 h, (B) 600 °C, 3 h and (C) 700 °C, 3h at Al:K atomic molar ratios of (a) 10:1; (b) 3:1; (c) 1:1; (d) 1:3 (the dot lines in (B) are the blank test results of catalysts prepared with a Al:K molar ratio of 3:1).

of calcination temperatures and Al:K molar ratios and the results are shown in Fig. 2.

Fig. 2A shows the TPR curves of catalysts calcined at 500 °C. The catalysts prepared with Al_2O_3/KOH showed a IOT of about 320 °C regardless of Al:K molar ratio. For the catalysts prepared with $Al(NO_3)_3/KNO_3$, however, the IOT was about 400 °C at a Al:K molar ratio of 10:1, and about 370 °C at Al:K molar ratios of 1:1 and 1:3. The catalysts prepared with Al_2O_3/KNO_3 displayed the IOTs of 338, 338 and 350 °C at Al:K molar ratios of 10:1, 1:1 and 1:3, accordingly. This investigation result confirms that the calcination temperature has greater effect on the catalytic activities of the catalysts prepared with $Al(NO_3)_3/KNO_3$.

When the catalysts were calcined at 600 °C, the catalytic activities of all catalysts were significantly improved by showing a lower IOT (Fig. 2B). The catalyst prepared with Al_2O_3/KOH at a Al:K molar ratio of 10:1 displayed an IOT of about 326 °C. The IOT was reduced to about 305 °C with increasing K^+ content to Al:K molar ratio of 1:1, while the IOT increased slightly with further increase of K^+ content in the catalyst. For the catalysts prepared with $Al(NO_3)_3/KNO_3$, the IOT was gradually reduced with increasing K^+ content from Al:K molar ration of 10:1 to 1:1, where the lowest IOT of 310 °C was reached, followed by a slight increase of IOT at a Al:K molar ratio of 1:3. For the catalysts prepared with Al_2O_3/KNO_3, the IOT was about 345 °C at a Al:K molar ratio of 10:1. However, the IOT was reduced to about 330 °C at a Al:K molar ratio of 3:1 and further increase of K^+ content caused a limited effect on IOT. It was also noticed that the catalysts prepared with all precursors exhibited the CO_2 evolution processes at the low temperature range. Therefore, the catalysts without coating soot were tested to obtain the blank TPR profiles (dot line in Fig. 2B) before the catalytic activity measurement. The major CO_2 production process was in the range from 100 to 300 °C. Even so, the catalyst prepared with Al_2O_3/KOH displayed the strongest CO_2 evolution process ascribed to the CO_2 absorption through bicarbonate species formation with the presence of water and K^+ as found in other catalyst systems studied previously [8,32].

When the catalysts were calcined at 700 °C, the catalytic activities of all catalysts were severely deteriorated as demonstrated by a noteworthy increase of IOT to about 350 °C (Fig. 2C). The catalysts prepared with Al_2O_3/KOH and $Al(NO_3)_3/KNO_3$ behaved in the same manner catalytically by showing a similar IOT and peak temperature, regardless of Al:K molar ratio. The catalysts prepared by Al_2O_3/KNO_3 showed a poor catalytic activity (IOT is about 370 °C.) when a small amount of K^+ was added at Al:K of 10:1, while a better catalytic activity was observed at a Al:K molar ratio of 1:3. Nevertheless, the catalytic activities of the catalysts calcined at 700 °C were less affected by K^+ content variation. Therefore, the optimal calcination temperature is 600 °C and the highest activities are obtained at Al:K molar ratios of 1:1, 1:1 and 3:1 for the catalysts prepared with Al_2O_3/KOH, $Al(NO_3)_3/KNO_3$ and Al_2O_3/KNO_3, correspondingly.

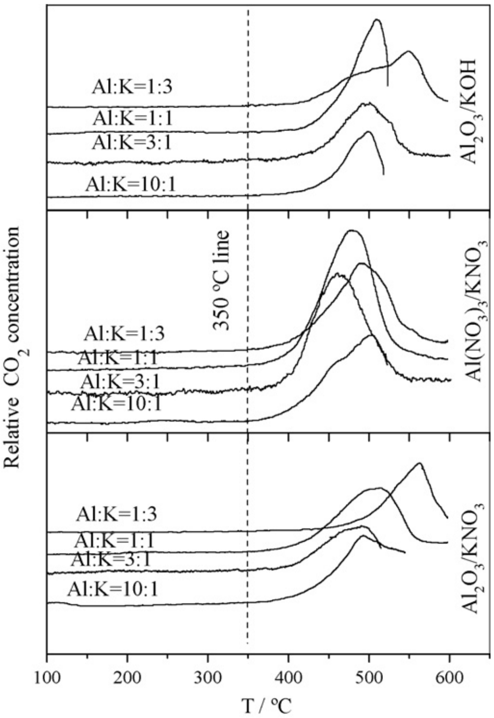

Fig. 3. Profiles of the catalysts prepared with Al_2O_3/KNO_3, $Al(NO_3)_3/KNO_3$ and Al_2O_3/KNO_3 precursor combinations after heat-treatment at 600 °C for 48 h.

In practical application, the catalysts will work at high temperature for a long time, and hence they should possess not only a good catalytic activity but also a high thermal stability. In order to exam their thermal stability, the catalysts were heat-treated at 600 °C for 48 h followed by TPR measurements. As shown in Fig. 3, the catalysts prepared with Al_2O_3/KOH and $Al(NO_3)_3/KNO_3$ displayed the IOTs of about 370 and 350 °C, respectively regardless of Al:K molar ratio. Nevertheless, the catalyst prepared with Al_2O_3/KOH at Al:K molar ratio of 1:3 behaved a slow oxidation rate as indicated by a higher peak temperature. The catalysts prepared by Al_2O_3/KNO_3 exhibited a comparable catalytic activity when Al:K molar ratios were 10:1 and 1:1. However, when more K^+ was added in the catalyst at a Al:K molar ratio of 1:3, the catalytic activity was significantly reduced by showing an IOT of about 430 °C. This study result proposes that high K^+ content in the catalyst could result in a poor thermal stability.

The active compounds responsible for the catalytic effect of the catalysts prepared by $Al(NO_3)_3/KNO_3$ were analyzed by XRD studies and the results are shown in Fig. 4. It can be seen from this figure that only Al_2O_3 and KNO_3 were identified and their contents decreased and increased, respectively with increasing KNO_3 content in the starting materials when the catalysts were calcined at 600 °C. The catalyst with a Al:K molar ratio of 1:1 and calcined at 700 °C displayed an identical diffraction pattern to that of the catalyst calcined at 600 °C suggesting that KNO_3 could be maintained in the composite structure at such a high temperature for as long as 3 h. The thermal stability of KNO_3 mixed with metal oxides up to 600 °C has also been found in the KNO_3/La_2O_3 [15], KNO_3/V_2O_5 and KNO_3/CeO_2 systems [32]. After heat-treatment at 600 °C for 48 h, however, only very weak diffraction peaks from KNO_3 were detected in the catalyst. The lack of Al_2O_3 detection by XRD could be due to the formation of amorphous phase resulting from the reaction

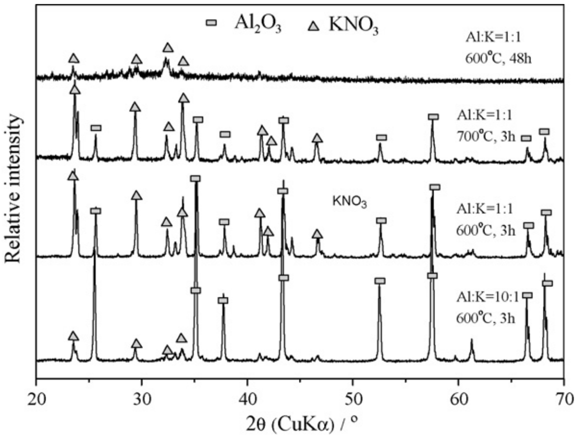

Fig. 4. XRD patterns of the catalysts prepared by $Al(NO_3)/KNO_3$ at various conditions.

between Al_2O_3 and K^+. Furthermore, it can be concluded that the improvement of catalytic activity of the catalyst with a Al:K molar ratio of 10:1 and activity deterioration of the catalyst with a Al:K molar ratio of 1:1 after calcinations at 700 °C or aging at 600 °C were due to their similar catalyst compositions resulting from the formation of amorphous phase produced by the reaction between Al_2O_3 and KNO_3 and loss of active compound KNO_3. Indeed, these catalysts behaved a similar catalytic activity after high temperature treatment.

XRD analysis results of the catalysts prepared by Al_2O_3/KOH at various conditions are shown in Fig. 5. At calcination temperature of 600 °C, only diffraction peaks from Al_2O_3 were detected from the catalyst at a Al:K molar ratio of 3:1. The lack of K^+ detection means most likely that K^+ has penetrated into the crystal structure of Al_2O_3 to form a kind of solid solution. With decreasing the Al:K molar ratio to 1:1, the diffraction peaks from Al_2O_3 were considerably weakened, while new diffraction peaks from $K_2Al_2O_4{\cdot}3H_2O$ and $K_2Al_2O_4$ were detected. At a Al:K molar ratio of 1:3, the Al_2O_3 phase disappeared, while $K_2Al_2O_4{\cdot}3H_2O$ and a small amount of $K_2CO_3{\cdot}1.5H_2O$ were identified in the catalyst. It was also noticed that the catalysts (Al:K = 1:1) heat-treated at 600 °C for 48 h, 500 °C for 3 h and 700 °C for 3 h had identical crystalline phases of K_3AlO_3 and $K_2CO_3{\cdot}1.5H_2O$ and showed the IOTs of 370, 350 and 320 °C, respectively. $K_2CO_3{\cdot}1.5H_2O$ in their structures as seen from XRD patterns should be, at least partially, responsible to their catalytic activities because K_2CO_3 has a good catalytic activity of soot oxidation by showing an IOT of about 310 °C [33]. The effect of K_3AlO_3 on the catalytic activity of catalysts is not clear at present, and more studies are needed to make it clear. However, the distribution states of K_3AlO_3 and K_2CO_3 within the catalysts calcined at different conditions should cause different catalytic activities of these catalysts. The catalyst (Al:K = 1:3) calcined at 700 °C had the $K_2Al_2O_4{\cdot}3H_2O$, $K_2Al_2O_4$ and a small amount of un-identified phases in the structure. Since the catalysts (Al:K = 1:3) calcined at 600 or 700 °C for 3 h have major crystalline phase of $K_2Al_2O_4{\cdot}3H_2O$ in their structure and demonstrated the IOTs of about 320 and 350 °C, respectively, it is safe to propose that $K_2Al_2O_4{\cdot}3H_2O$ is a active compound of soot oxidation. The formation of $K_2CO_3{\cdot}1.5H_2O$ in the catalysts suggests that there is reaction between CO_2 and K^+ taking place during calcinations process. K_2CO_3 would react with water and CO_2 in air forming $K_2CO_3{\cdot}1.5H_2O$ or potassium bicarbonate species. This could explain why these catalysts have a stronger CO_2 evolution process during heating than the catalysts prepared by $Al(NO_3)/KNO_3$ and Al_2O_3/KNO_3.

Fig. 6 shows the XRD patterns of the catalysts prepared by Al_2O_3/KNO_3 at various Al:K molar ratios. It can be clearly seen from this figure that the main compounds in the catalysts are Al_2O_3 and KNO_3 when the catalysts were calcined at 600 °C. Al_2O_3 and KNO_3 contents decreased and increased separately with decreasing Al:K molar ratio from 3:1 to 1:3 when the catalysts were calcined at 600 °C for 3 h. However, KNO_3 content was significantly reduced in the catalysts (Al:K = 3:1) when they were heat-treated at 600 °C for 48 h or 700 °C for 3 h. A much weaker signal from KNO_3 in the catalyst calcined at 700 °C for 3 h indicates a higher decomposing rate of KNO_3 at 700 °C. The XRD study results suggest that the catalysts prepared by $Al(NO_3)_3/KNO_3$ and Al_2O_3/KNO_3 have the main crystalline

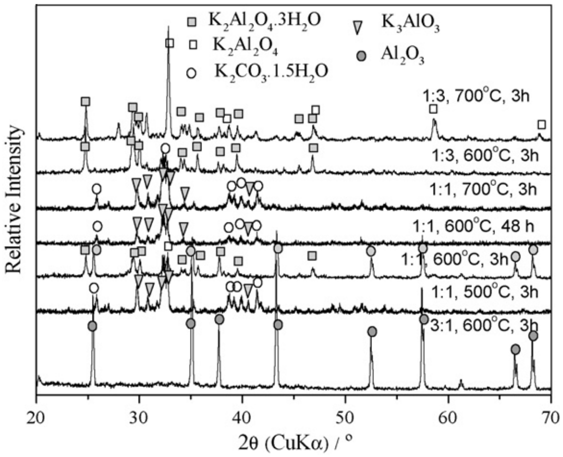

Fig. 5. XRD patterns of the catalysts prepared by Al_2O_3/KOH at various conditions.

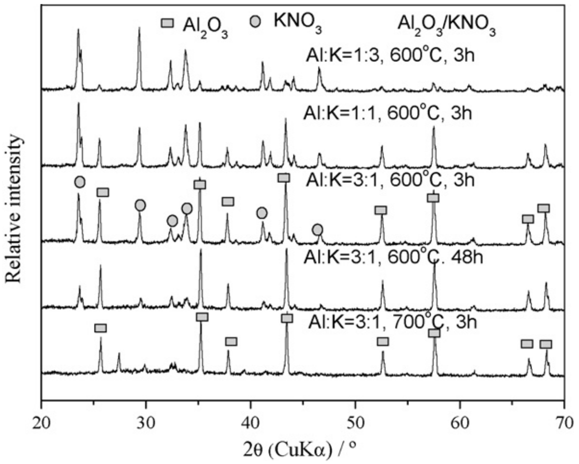

Fig. 6. XRD patterns of the catalysts prepared by Al_2O_3/KNO_3 at various conditions.

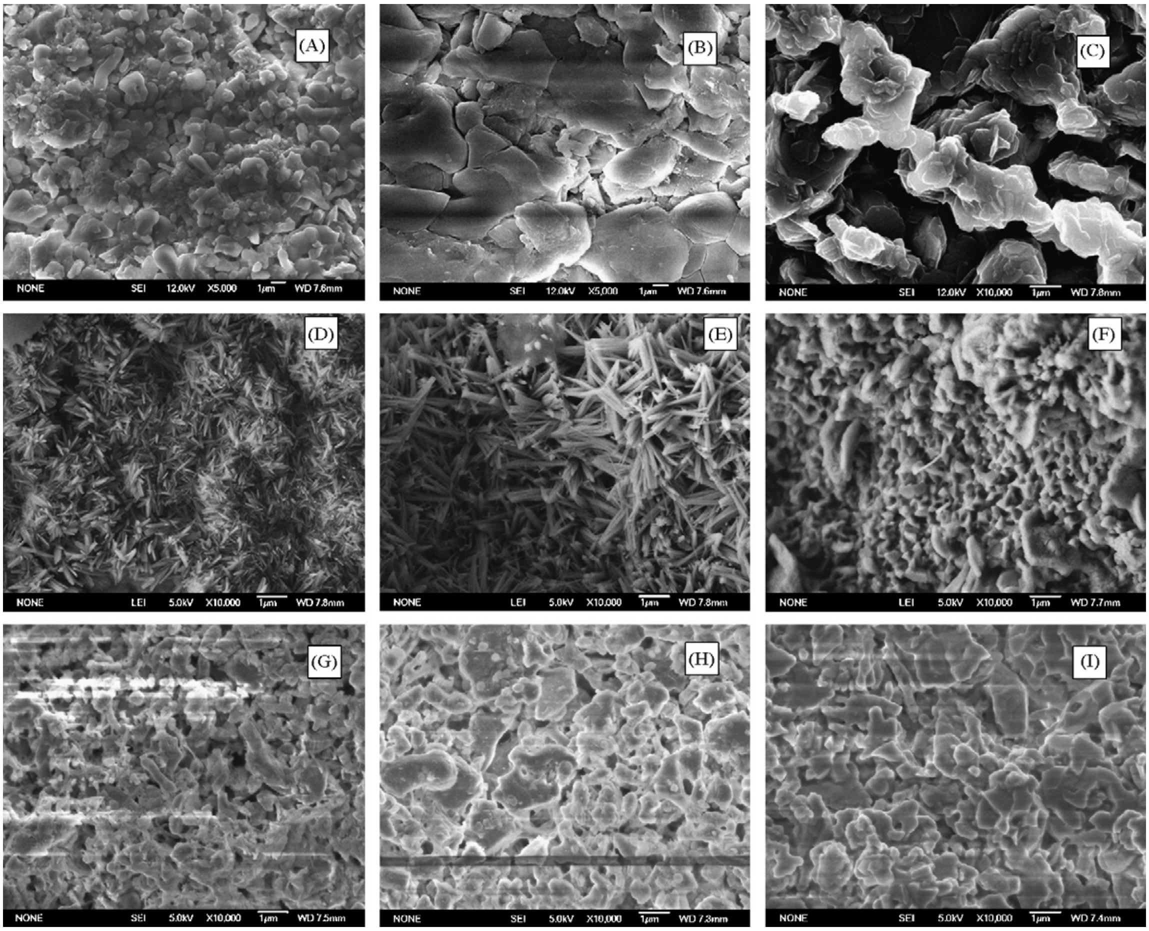

Fig. 7. Morphologies of the catalysts prepared with different precursors. Al_2O_3/KOH (Al:K = 1:1, (A) 600 °C, 3 h; (B) 700 °C, 3 h; (C) 600 °C, 48 h), $Al(NO_3)_3/KNO_3$ (Al:K = 1:1, (D) 600 °C, 3 h; (E) 700 °C, 3 h; (F) 600 °C, 48 h) and Al_2O_3/KNO_3 (Al:K = 3:1, (G) 600 °C, 3 h; (H) 700 °C, 3 h; (I) 600 °C, 48 h).

phases of KNO_3 and Al_2O_3 and high working temperatures may result in the loss of active compound KNO_3.

SEM analysis results of the catalysts prepared by Al_2O_3/KOH (Al:K = 1:1), $Al(NO_3)_3/KNO_3$ (Al:K = 1:1) and, Al_2O_3/KNO_3 (Al:K = 3:1) at various conditions are shown in Fig. 7. It can be seen from this figure that the catalyst prepared by Al_2O_3/KOH at a calcination temperature of 600 °C has a particle size of about 1–2 μm. However, the particles grew significantly when the calcination temperature was 700 °C, implying that the surface area of the catalyst was dramatically reduced. Aging at 600 °C for 48 h resulted in considerable sintering of the catalyst and loss of active compound K_2CO_3 leaving holes on the catalyst surface. It is then clear that the deterioration of catalytic activity of the catalysts calcined at 700 °C for 3 h and treated at 600 °C for 48 h was attributed to the loss of surface area and active compounds, respectively. The catalysts prepared by $Al(NO_3)_3/KNO_3$ (Al:K = 1:1) showed a whisker-like morphology when the calcination temperatures were 600 and 700 °C. Nevertheless, high calcination temperature of 700 °C led to a bigger whisker and looser structure, and hence a weaker catalytic activity due to the loss of surface area of catalyst; even it has a similar chemical composition to that of the catalyst produced at 600 °C. The catalyst became significantly dense, attributable to the formation of amorphous phase after aging at 600 °C for 48 h leading to a weaker catalytic activity because of loss of surface area and active compound, KNO_3. For the catalysts prepared by Al_2O_3/KNO_3, the particle size increased slightly after heat-treatment at 600 °C for 48 h or at 700 °C for 3 h as shown in Fig. 7G–I. The loss of KNO_3 caused no significant change on the surface morphology of the catalyst because of its low content in the catalyst.

4. Conclusions

The calcination temperature, Al:K molar ratio and precursor combination have profound effect on the catalytic activity of resulting Al_2O_3–K catalysts. The optimal calcination temperature is 600 °C and the highest activities were obtained at Al:K molar ratios of 3:1, 1:1 and 3:1 for Al_2O_3/KNO_3, $Al(NO_3)_3/KNO_3$ and Al_2O_3/KOH precursor combinations, respectively. The active compound in the catalysts prepared by Al_2O_3/KNO_3 and $Al(NO_3)_3/KNO_3$ was KNO_3 exclusively. However, the catalytic activity of the catalysts prepared by Al_2O_3/KOH was affected by the $K_2Al_2O_4$ and K_2CO_3 compounds. The catalysts prepared by all precursor combinations behaved in a comparable thermal stability. High temperature aging of the catalysts would result in the loss of surface area and/or active compounds, and hence the deterioration of catalytic activity.

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