

Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil

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Abstract

Biodiesel fuel, a promising alternative diesel fuel produced by a catalytic transesterification of vegetable oils, has become more attractive recently because of its environmental concerns and the fact that it is made from renewable resources. In this work, the transesterification of soybean oil with methanol has been studied in a heterogeneous system, using alumina loaded with potassium iodide as a solid base catalyst. After loading KI of 35 wt.% on alumina followed by calcination at 773 K for 3 h, the catalyst gave the highest basicity and the best catalytic activity for this reaction. The catalysts were characterized by means of XRD, IR, SEM and the Hammett indicator method. Moreover, the dependence of the conversion of soybean oil on the reaction variables such as the catalyst loading, the molar ratio of methanol to oil and the reaction time was studied. The conversion of 96% was achieved under the optimum reaction conditions. Besides, a correlation of the catalyst activity for the transesterification reaction with its basicity was proposed.

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1. Introduction

Due to the predicted shortness of conventional fuels and environmental concerns, a search for alternative fuels has gained recent significant attention. As the calorific value of vegetable oils is comparable to that of diesel, they could be used as fuels in compression ignition engines. However, their direct use in injection diesel engines is problematic mainly because of their high viscosity and low volatility. Indeed, the viscosity of vegetable oils is about ten times higher than that of diesel. As a result, the vegetable oils could cause poor fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats resulting in serious engine fouling. The commonly employed methods for reducing the viscosity of vegetable oils are blending with diesel, emulsification, pyrolysis, cracking and transesterification. Among these, transesterification of vegetable oils to methyl esters appears to be the best method [1].

The transesterification of vegetable oils is a catalytic transesterification reaction where a triglyceride reacts with methanol

producing glycerine and a mixture of fatty acid esters. The result is that triglyceride molecules, which are long and branched, are transformed into smaller esters whose size and properties are similar to those of diesel oils. These esters have significant potential as an alternative diesel fuel (better known as biodiesel) both in neat forms or blended with conventional diesel fuels. Biodiesel is characterized by excellent properties as diesel engine fuels and thus can be used in compression-ignition (diesel) engines with little or no modifications. Besides, it also effects a decrease in emissions of SO_x, CO, unburnt hydrocarbons and particulate matter during the combustion process when compared with fossil fuels [2,3].

Biodiesel is usually prepared in the presence of homogeneous base or acid catalysts. The acid-catalyzed process often uses sulfonic acid and hydrochloric acid as catalysts; however, the reaction time is very long (48–96 h) even at reflux of methanol, and a high molar ratio of methanol to oil is needed (30–150:1, by mol) [4–6]. Potassium hydroxide, sodium hydroxide and their carbonates, as well as potassium and sodium alkoxides such as NaOCH₃, are usually used as base catalysts for this reaction [7–9]. As the catalytic activity of a base is higher than that of an acid and acid catalysts are more corrosive, the base catalysis is

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preferred to acid catalyzed routes, and is thus most often used commercially.

However, in this conventional homogeneous method removal of these catalysts after reaction is technically difficult and a large amount of wastewater was produced to separate and clean the catalyst and the products. Therefore, conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts. The replacement of homogeneous catalysts by heterogeneous catalysts would have various advantages, most important being the application of easier working up procedures, the easy catalyst separation from the reaction mixture and the reduction of environment pollutants. At the laboratory scale, many different heterogeneous catalysts have been developed to catalyze the transesterification of vegetable oils with methanol. For example, Beynese et al. [10] reported the use of EST-4 and EST-10 catalysts to provide conversions of 86% and 53%, respectively, at 493 K and 1.5 h reaction time. Besides, Suppes et al. [11] achieved conversions of 78% at 513 K and >95% at 533 K for the transesterification of vegetable oils using calcium carbonate rock as a catalyst. Both the above studies required temperatures higher than 473 K to achieve high conversions within the time scales of the experiments. More recently, Kim et al. [12] prepared a solid superbase of Na/NaOH/ γ -Al₂O₃, which showed almost the same catalytic activity under the optimized reaction conditions as that of the conventional homogeneous NaOH catalyst. Vegetable oils and methanol are not miscible and form two liquid layers upon their initial introduction into reactor. In most of the experiments using heterogeneous catalysts, the reaction proceeded at a relatively slow rate compared to those conducted with homogeneous base catalysts such as KOH and NaOH. These slow reaction rates are due to diffusion problems since these heterogeneous media behave as a three-phase system (oil/methanol/catalyst). In spite of this, heterogeneous catalysts could improve the synthesis methods for the development of an environmentally benign process and the reduction of production cost.

Yamaguchi et al. [13] reported that the catalysts, which were prepared by loading alkali metal compounds such as KNO₃ on alumina, followed by heating at 773–873 K, were very strongly basic catalysts and active for the isomerization of *cis*-but-2-ene at 273 K and, the activity of the catalyst was also confirmed by other researchers [14]. These materials did not show any strong basicity before activation, which made them distinguished from other solid bases for industrial applications, since the contamination of CO₂ from atmosphere could be avoided. In the *in situ* activation prior to reaction, unusually strong basic sites such as K₂O [14] were formed on the composites resulting from the decomposition of loaded KNO₃ and had retained high efficiency in the catalytic processes. By drawing on this, it can then be supposed that loading KI on alumina followed by calcination at a high temperature could also generate strong basic sites and this material can be used for base-catalyzed reactions because of easy thermal decomposition of KI to K₂O in air. In this work, the KI/Al₂O₃ sample was tested as a heterogeneous catalyst for the transesterification of soybean oil with methanol. The catalytic efficiency in this reaction was estimated regarding the conversion of soybean oil to methyl esters. XRD, IR, SEM, DTA-TG and the

Hammett indicator method were employed for the catalyst characterizations. Besides, the effect of the reaction variables such as the ratio of methanol to oil, the reaction time and the catalyst amount on the conversion to methyl esters was investigated. Further, a correlation between the basicity of the catalysts and their catalytic activity towards the transesterification of soybean oil was also proposed.

2. Experimental

2.1. Preparation of the catalyst

All the catalysts were prepared by impregnation of alumina with an aqueous solution of potassium compounds. For this purpose, 10 g of the support was impregnated with 30 mL of the potassium compounds solution and water was removed in a rotary evaporator at 353 K until dryness. This impregnate was dried in an oven at 393 K overnight and then the solid was calcined in a muffle furnace at designated temperatures for 3 h before use for the reaction.

2.2. Catalyst characterizations

Base strength of the samples (H_-) was determined by using Hammett indicators [15–17]. About 300 mg of the sample was shaken with 1 mL of a solution of Hammett indicators diluted in 10 mL methanol and left to equilibrate for 2 h after which no further colour changes were observed. The colour on the catalyst was then noted. The following Hammett indicators were used: bromthymol Blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), 2,4-dinitroaniline ($H_- = 15.0$) and 4-nitroaniline ($H_- = 18.4$). While Hammett indicator measurements are conventionally performed using non-polar solvents, it was deemed appropriate to use methanol in this instance, thus allowing a better measure of the base strengths under reaction conditions where methanol is employed as both solvent and reactant. The base strengths are quoted as being stronger than the weakest indicator that exhibits a colour change, but weaker than the strongest indicator that produces no colour change. To measure the basicity of solid bases, the method of Hammett indicator-benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration was used.

Powder X-ray diffraction measurements were conducted on a Philips X, Pert Pro MPD X-ray diffractometer using a radiation source of Cu K α ($\lambda = 0.154$ nm) at 40 kV and 50 mA. Data were collected over a 2θ range of 10–80° with a step size of 0.017° at a scanning speed of 5° min⁻¹. The XRD phases were identified using the power diffraction file (PDF) database (JCPDS, International Center for Diffraction Data)

Thermal decomposition of KI/Al₂O₃ samples was evaluated by thermogravimetric analysis (TG) and differential thermal analysis (DTA) carried out on a Shimadzu DT-40 instrument operating under a flow of air at a 10 K min⁻¹ heating rate up to 1069 K.

Scanning electron micrographs (SEM) were obtained on an AMRAY-1000B scanning electron microscope. The accelerating voltage was 20 kV.

The KBr pellet technique was applied for determining IR spectra of the samples. Spectra were recorded on a Shimadzu IR-Prestige-21 spectrometer with 4 cm^{-1} resolutions. The scanning range was from 400 to 4600 cm^{-1} .

2.3. Transesterification reaction

Commercial edible grade soybean oil was obtained from market. According to GC (Shimadzu DC-9A) analysis [18], the fatty acid consisted of palmitic acid 12.3%, stearic acid 5.8%, oleic acid 26.5%, linoleic acid 49.4% and linolenic acid 5.9%. The acid value was less than 0.1 mg KOH/g , and the average molecule weight was 874 g/mol , calculated from the saponification index ($SV = 192.6\text{ mg KOH/g}$).

A 250 mL one-necked glass flask equipped with a water-cooled condenser and a magnetic stirrer was charged with 16.0 g (18.3 mmol, calculated from the average molecular weight of the soybean oil) of soybean oil, different volumes of anhydrous methanol and varied amounts of freshly prepared catalyst. Each mixture was stirred vigorously at reflux of methanol for the required reaction time. The progress of the reaction was monitored by ^1H NMR spectroscopy (Bruker, 400 MHz). Normally, the reaction mixture was filtered and the liquid phase was washed three times with a saturated aqueous NaCl solution. The organic phase was separated by decantation, dried with anhydrous sodium sulfate and submitted to NMR analysis in CDCl_3 using TMS as internal standard. The conversion of the soybean oil to a mixture of methyl esters was determined by the ratio of the signals at 3.68 ppm (methoxy groups of methyl esters) and 2.30 ppm (α -carbon CH_2 groups of all fatty acid derivatives) according to Ref. [19].

3. Results and discussion

3.1. Screening of the catalyst

The catalytic activity screening of Al_2O_3 loaded with different potassium compounds in the soybean oil transesterification was performed. The results are summarized in Table 1. To make direct comparisons, the same reaction conditions, as shown in

Table 1
Catalytic activities and base strengths of alumina loaded with different potassium compounds

Catalysts	Basic strength	Conversion (%)
Al_2O_3	<7.2	No reaction
$\text{KF}/\text{Al}_2\text{O}_3$	$15.0 < H_- < 18.4$	85.8
$\text{KCl}/\text{Al}_2\text{O}_3$	<7.2	No reaction
$\text{KBr}/\text{Al}_2\text{O}_3$	$9.3 < H_- < 15.0$	16.7
$\text{KI}/\text{Al}_2\text{O}_3$	$15.0 < H_- < 18.4$	87.4
$\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$	$9.3 < H_- < 15.0$	48.0
$\text{KNO}_3/\text{Al}_2\text{O}_3$	$15.0 < H_- < 18.4$	67.4
$\text{KOH}/\text{Al}_2\text{O}_3$	$15.0 < H_- < 18.4$	80.2

Reaction conditions: methanol/oil molar ratio, 15:1; catalyst amount, 2 wt.%; reaction time, 6 h; methanol reflux temperature. All catalysts were activating at 773 K for 3 h before use for the reaction. The loading amount of potassium compounds was 2.1 mmol/g on alumina.

Table 1, were employed for each catalyst in all experiments. The reaction conditions were not optimized for the highest reaction yield; however, they provided a way to compare the activities of the catalysts. Obviously, it is observed from Table 1 that non-loaded alumina exhibited no activity. However, when potassium compounds were loaded on alumina and activated at high temperatures, the supported catalysts except $\text{KCl}/\text{Al}_2\text{O}_3$ showed catalytic activities. Thus, it is essential to support potassium compounds on alumina to generate the catalytic activities for the transesterification reaction. Among the catalysts tested, alumina loaded with KI, KF or KOH exhibited comparatively high activities, giving conversions higher than 80%. Especially, $\text{KI}/\text{Al}_2\text{O}_3$ demonstrated the superior catalytic activity compared to the other catalysts. When the transesterification was conducted over the $\text{KI}/\text{Al}_2\text{O}_3$ catalyst, the highest conversion of 87.4% was achieved. Over $\text{KNO}_3/\text{Al}_2\text{O}_3$, $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ and $\text{KBr}/\text{Al}_2\text{O}_3$ catalysts, however, the lower conversions in the range of 16–67.4% were obtained, attributable to their relatively low catalytic activities. Based on these results, the conversion to methyl esters over the catalysts is in the following order: $\text{KI}/\text{Al}_2\text{O}_3 > \text{KF}/\text{Al}_2\text{O}_3 > \text{KOH}/\text{Al}_2\text{O}_3 > \text{KNO}_3/\text{Al}_2\text{O}_3 > \text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3 > \text{KBr}/\text{Al}_2\text{O}_3$.

The base strengths of Al_2O_3 modified with different potassium compounds were measured by using Hammett indicators. As evident in Table 1, loading of KF, KNO_3 or KI on the surface of alumina could induce the base strength (H_-) in the range of 15.0–18.4. According to the definition of Tanabe [20], these samples can be assigned to strong bases. However, KBr or K_2CO_3 loaded on alumina generated the weaker basic sites with H_- in the range of 9.8–15.0. Taking both the base strength and the catalytic activity into account, we can conclude that the observed activities of alumina-supported catalysts seem to be related to their base strengths, i.e. the higher base strengths of the catalysts result in the higher conversions. In particular, the $\text{KCl}/\text{Al}_2\text{O}_3$ sample possessed the weakest base strength in the range of $H_- < 7.2$, consequently exhibiting no catalytic activity. Interestingly, for $\text{KCl}/\text{Al}_2\text{O}_3$, $\text{KBr}/\text{Al}_2\text{O}_3$ and $\text{KI}/\text{Al}_2\text{O}_3$ samples, the nature of anions significantly affected the base strength together with the catalytic activity. As far as the anion was concerned, the order of the catalytic activity is as follows: $\text{KI}/\text{Al}_2\text{O}_3 > \text{KBr}/\text{Al}_2\text{O}_3 > \text{KCl}/\text{Al}_2\text{O}_3$. This order is opposite to the order of their thermal stability in air, which probably suggests that their different catalytic activities should be attributed to their different decomposition extents in air, and therefore, the K_2O species derived from the decomposition process possibly being the main catalytically active species. But for the $\text{KF}/\text{Al}_2\text{O}_3$ sample, it has been reported that the F^- species is related to the catalytic activity [21–23]. As for the catalytic sites on $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ and $\text{KOH}/\text{Al}_2\text{O}_3$ samples, it can also be proposed that the K_2O species, which was possibly formed by thermal decomposition of the carbonates or by dehydroxylation of the OH groups, was at least a part of catalytically active sites [13,24]. As remarked above, it seems that the transesterification reaction needs strongly basic sites.

The effect of supports on the activity of the catalysts is shown in Table 2. Clearly, when KI was supported on different carriers, the base strengths and catalytic activities varied significantly. As

Table 2
Catalytic activities and base strengths of KI supported on the different carriers

Catalysts	Basic strength	Conversion (%)
KI/ZrO ₂	15.0 < H ₋ < 18.4	78.2
KI/ZnO	9.3 < H ₋ < 15.0	72.6
KI/NaX	9.3 < H ₋ < 15.0	12.9
KI/KL	9.3 < H ₋ < 15.0	28.3
KI/Al ₂ O ₃	15.0 < H ₋ < 18.4	87.4

Reaction conditions: methanol/oil molar ratio, 15:1; catalyst amount, 2 wt.%; reaction time, 6 h; methanol reflux temperature. All catalysts were activating at 773 K for 3 h before use for the reaction. The loading amount of KI was 35 wt.%.

listed in Table 2, KI/Al₂O₃ was the most active catalyst for the transesterification reaction, giving a conversion of 87.4%. Over KI/ZnO and KI/ZrO₂ catalysts, even though they possessed different centers of a base strength, the high conversions of 72.6% and 78.2% were also achieved, respectively. However, since the SiO₄ tetrahedra of zeolite hindered the formation of strongly basic sites [25], KI loaded on KL and NaX could induce a weak base strength (9.3 < H₋ < 15.0), and thereby, exhibiting lower catalytic activities; the conversions over them were lower than 30%. Thus, alumina can be regarded as the best support. Moreover, even though the base strength of KI/ZnO, KI/NaX and KI/KL samples was the same, the great difference in catalytic activities was seen among them. Therefore, it is very likely that the activity of the catalysts is strongly affected not only by the strength of basic sites but also by the amount of basic sites, and therefore, interpretation of the catalytic activity is difficult. At present time, we do not completely understand the result.

As just discussion above, KI/Al₂O₃ manifested the best catalytic activity. On account of the high activity of the catalysts in the transesterification reaction, KI/Al₂O₃ was, therefore, selected for further investigation and its properties were studied in more detail.

3.2. Basicity determination of the catalyst

The basicity of KI/Al₂O₃ samples with different loading amounts of KI is shown in Fig. 1. As can be seen, when the

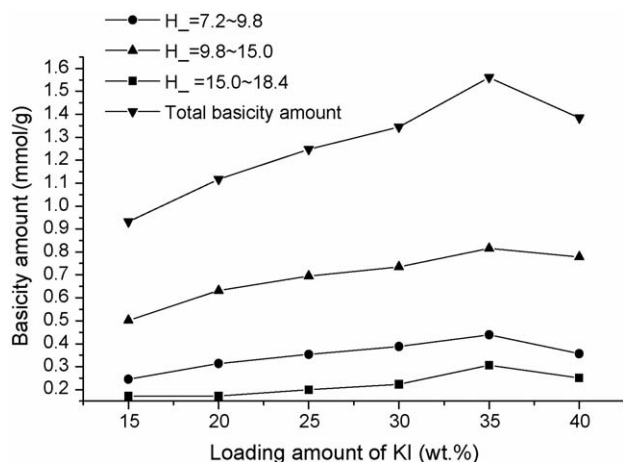


Fig. 1. Basicity of KI/Al₂O₃ samples with different loading amounts of KI and after being calcined at 773 K.

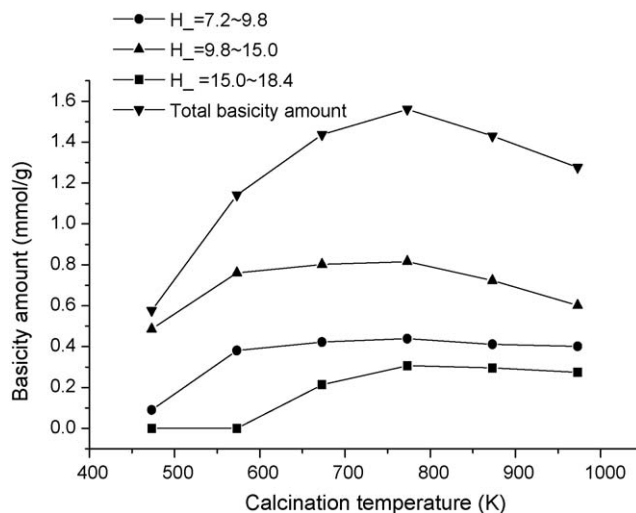


Fig. 2. Basicity of 35% KI/Al₂O₃ sample calcined at different temperatures.

amount of loaded KI increased from 15 to 35 wt.%, the catalyst basicity (total basicity) was markedly increased and came up to the maximum value at loading KI of 35 wt.%, but the strength of the basic sites was kept unchanged (H₋ = 15.0–18.4). However, with further increase in the amount of loaded KI, the basicity was decreased even though the basic sites were of equal strength, which resulted in a drop of the catalytic activity towards the reaction as observed in Fig. 7. This is presumably due to the coverage of surface basic sites by the excessive KI. These sites are, thus, inaccessible to incoming reactants when the amount of loaded KI exceeded 35 wt.%. Moreover, the basicity of 35 wt.% KI/Al₂O₃ sample calcined at different temperatures was measured by the same method, and the results are presented in Fig. 2. From this figure, it can be observed that the maximum basicity (total basicity), reaching 1.5607 mmol/g, was obtained at a calcination temperature of 773 K. But, a low level of basicity was observed below 673 K and above 873 K. Obviously, the basicity changes with calcination temperatures parallel the changes in the catalytic activity for the transesterification reaction, as illustrated in Fig. 8. However, the measured basicity of KI/Al₂O₃ catalysts was lower than the corresponding calculated value if all of KI was decomposed and converted to K₂O (data not shown). Such a result probably showed that the loaded KI was not totally decomposed to K₂O and/or was not decomposed to create the same type of basic sites. On the other hand, as we can see from Figs. 1 and 2, the main basic sites with H₋ in the range of 7.2–9.8 and 9.8–15.0 and the fewer basic sites with H₋ in the range of 15.0–18.4 were observed. Consequently, it is likely that at least two types of basic sites are expected to be generated on KI/Al₂O₃.

It should be pointed out that the measurement of base site distributions of porous catalysts by the Hammett indicator titration method remains controversial due to solvent–support interactions and the accessibility of the probe molecule within micropores [15,26,27]. Nevertheless, the data obtained by using Hammett indicator titration are in good agreement with the catalytic findings which will be discussed in detail elsewhere.

3.3. Catalyst characterizations

3.3.1. XRD patterns

X-ray diffraction patterns of KI/Al₂O₃ samples with various loading amounts of KI, are given in Fig. 3. As can be seen, when the loading amount of KI was below 30 wt.% (curves a–c in Fig. 3), only diffraction peaks ($2\theta = 37.0^\circ$, 46.0° and 66.7°) assigned to the amorphous Al₂O₃ support were registered on the XRD patterns, and neither any characteristic peaks of KI nor any new species such as K₂O was observed, indicating the good dispersion of KI on alumina in the form of a monolayer due to the interaction between KI and the surface of the support. When the amount of loaded KI was raised to 35 wt.%, the characteristic XRD peaks of KI appeared on the patterns (curves d and e in Fig. 3), and their intensities grew with increasing amount of loaded KI, implying that a residual phase of KI remained on the composite. Based on these XRD results, it is inferred that the spontaneous dispersion capacity of KI on alumina was between 35 and 40 wt.%. The XRD-undetectable phase of KI may have dispersed onto the surface of alumina as a monolayer [28]. For those loaded with potassium iodide at more than the spontaneous dispersion capacity on alumina, the residual bulk phase of KI remained on the composite. Accordingly, it is reasonable to imagine that only a part of the loaded KI could be decomposed under the activation conditions, as suggested by the results of the basicity measurements. Moreover, on the patterns of 35 wt.% KI/Al₂O₃ sample calcined at 773 K (curve d in Fig. 3), new diffraction lines which appeared at 2θ of 38.0° and 55.0° , were ascribed to K₂O species. It is very likely that the high basicity together with the high activity of the catalyst, as evident in Figs. 1 and 7, may be partially due to this K₂O phase since a relationship was observed between the K₂O species and

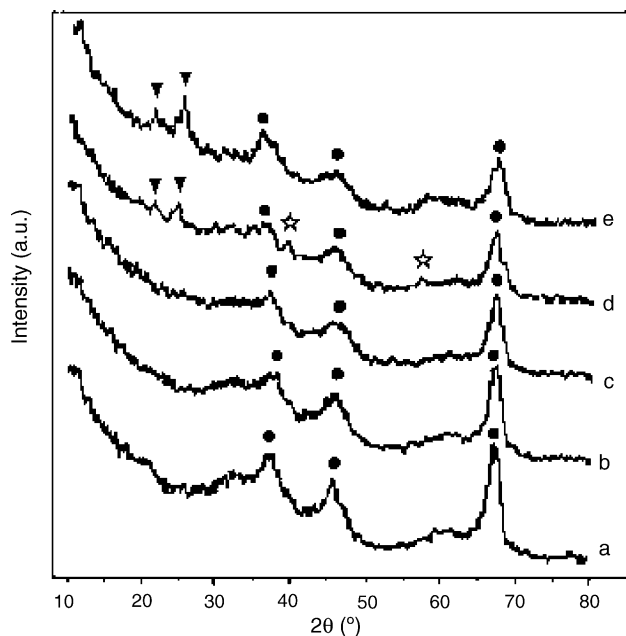


Fig. 3. XRD patterns for samples calcined at 773 K for 3 h: (a) 15% KI/Al₂O₃, (b) 25% KI/Al₂O₃, (c) 30% KI/Al₂O₃, (d) 35% KI/Al₂O₃ and (e) 40% KI/Al₂O₃. (▼) KI; (●) Al₂O₃; (☆) K₂O.

the basicity or the catalytic activity. On the other hand, the characteristic peaks of alumina ($2\theta = 37.0^\circ$, 46.0° and 66.7°) were almost unchanged on the XRD patterns regardless of the loading amount of KI, indicating that even though the KI was in the crystalline form at higher loading amounts of KI, the alumina still retained its amorphous structure for these loading amounts and a calcination temperature of 773 K, which resulted in the high surface area of the catalysts that were necessary for catalysis. SEM photographs will further confirm this result.

There are many defects or vacancies in the structure of alumina, resulting from the dehydration of surface hydroxyl groups, so that the dispersion of salts on alumina is actually the incorporation of cations into the vacancies by strong salt–support interactions [29]. It is noteworthy that the solid-state reaction between the guest compound and the surface of the support in the activation process is favorable for the catalyst to get a high catalytic activity. In the case of KI/Al₂O₃, the K⁺ ion of KI could insert in the vacant sites of alumina, accelerating dissociative dispersion and decomposition of KI to form basic sites in the activation process. The more potassium compounds are loaded on the alumina, the more free vacancies decrease, which results in the surface enrichment of potassium species that is probably considered to be the active sites for base-catalyzed reactions. When the amount of potassium cations loaded on alumina was below the saturation uptake of K⁺, it could be well dispersed. As a result, the number of basic sites together with the activities of the catalysts would increase with the potassium contents. However, if alumina was loaded with too much KI, the KI could not be well dispersed and, for this reason, not all but only a part of the loaded KI could be decomposed. Moreover, as mentioned in the preceding sections, the excess KI would cover the basic sites on the surface of the catalysts resulting in a lowered catalytic activity.

3.3.2. SEM analysis

The scanning electron micrographs of the samples are presented in Fig. 4. The SEM photographs of Al₂O₃ and KI/Al₂O₃ samples showed the crystallites of 2–12 μm size and nearly of hexahedron shape. Evidently, as shown in Fig. 4, no important difference was observed between Al₂O₃ and KI/Al₂O₃ samples, thus suggesting a good dispersion of KI on the surface of Al₂O₃. Based on these results, after loading of KI, Al₂O₃ retained its structure that was important for catalysis and therefore the potassium species was found highly distributed upon the surface of the support.

3.3.3. Thermal analysis

The thermal behavior of 35 wt.% KI/Al₂O₃ sample is illustrated in Fig. 5. This figure showed two weight losses. The first one in the range of 317–486 K, which was accompanied by an endothermic event, corresponded to the removal of the surface loosely physisorbed water. The second one overlapping a broad endothermic peak in a wide temperature range 486–1069 K, was probably attributed mainly to the combination of the decomposition of KI, the solid-state reaction of the guest compound with the support and the dehydration of Al–OH groups of alumina. However, in the case of KF/Al₂O₃ samples reported previously,

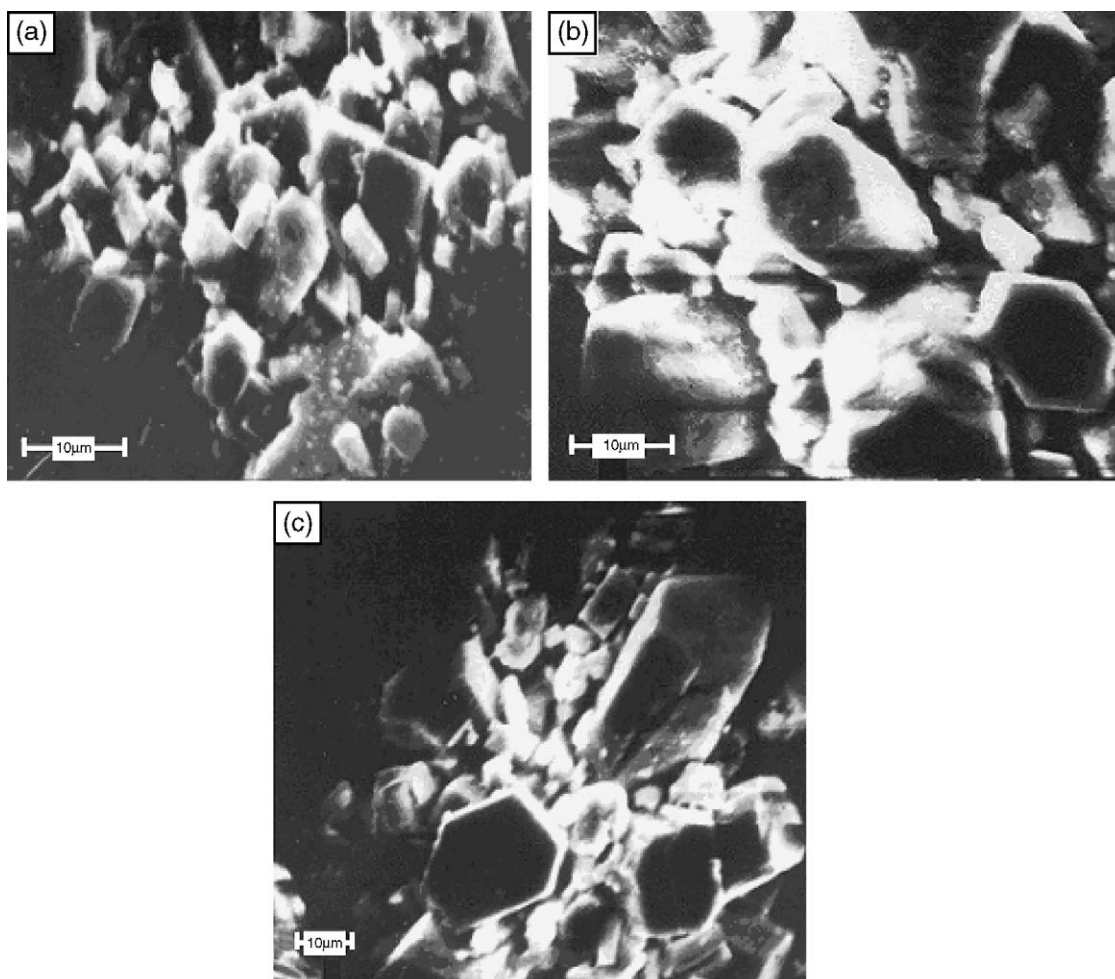


Fig. 4. Scanning electron micrographs (SEM) of the samples: (a) Al_2O_3 without calcination, (b) 30 wt.% $\text{KI}/\text{Al}_2\text{O}_3$ calcined at 773 K and (c) 35 wt.% $\text{KI}/\text{Al}_2\text{O}_3$ calcined at 773 K.

no F evolution was detected during the heating, and a very broad exothermic peak was observed due to a solid-state reaction of the fluorides with the support [30].

3.3.4. Infrared spectroscopy analysis

The investigation of $\text{KI}/\text{Al}_2\text{O}_3$ samples was conducted via IR spectroscopy as shown in Fig. 6. All the samples showed a very

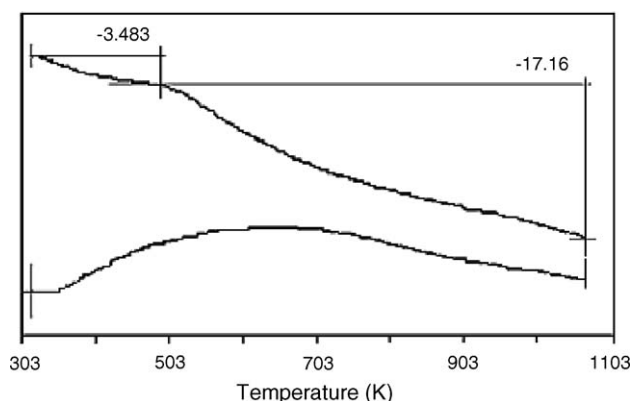


Fig. 5. DTA-TG curves of 35 wt.% $\text{KI}/\text{Al}_2\text{O}_3$ sample.

intense broad band at approximately 3480 cm^{-1} that could be ascribed to the ν_{OH} stretching vibration of the hydroxyl groups attached to Al_2O_3 . Besides, the minor absorption peak at about 1635 cm^{-1} may be assigned to the δ_{OH} bending vibration mode of H_2O molecules absorbed from air [31]. Moreover, with the increase of calcination temperature, the 1635 cm^{-1} band became weaker and, finally disappeared (curve a–e in Fig. 6).

Additionally, there were two bands at 1550 and 1410 cm^{-1} , which were probably attributed to the vibration of CO_3^{2-} [23,32]. These two bands became stronger when the calcination temperature rose from 383 to 873 K (curves a–e in Fig. 6). The carbonates were supposed to be formed by the reaction of K_2O with carbon dioxide during the calcination procedure in air. However, as shown in Table 1, the catalytic activity of $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ sample for the transesterification reaction was much lower than that of $\text{KI}/\text{Al}_2\text{O}_3$, suggesting that the carbonate species was not a catalytically active species for the reaction.

Furthermore, the broad band at around 3480 cm^{-1} could be partly assigned to the stretching vibration of Al-O-K groups [33–35]. According to Stork and Pott [36], on the surface of fully hydroxylated alumina, K^+ ions could replace the protons of isolated hydroxy groups to form Al-O-K groups in the acti-

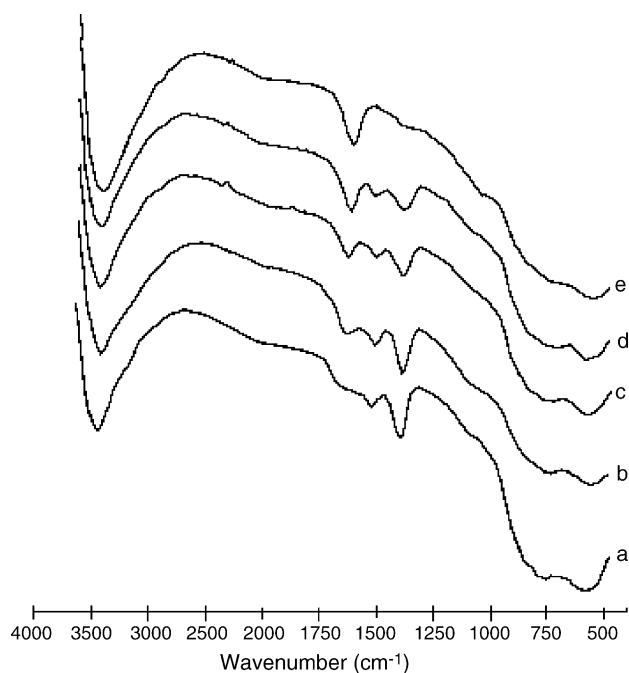


Fig. 6. FTIR spectra of 35 wt.% KI/Al₂O₃ sample calcined at different temperatures for 3 h: (a) 873 K, (b) 773 K, (c) 673 K, (d) 473 K and (e) 383 K.

vation process, which were probably considered to be the active species of this catalyst.

3.4. Influence of catalyst preparation conditions

In order to study the effect of KI loading amounts of the catalysts on their catalytic activities, a series of KI/Al₂O₃ samples with the loading amount of KI ranging from 15 to 40 wt.%, were prepared and employed to catalyze the transesterification reaction. The results are presented in Fig. 7. As seen from this figure, as the loading amount of KI was raised from 15 to 35 wt.%, the conversion was increased and the highest conversion of 87.4%

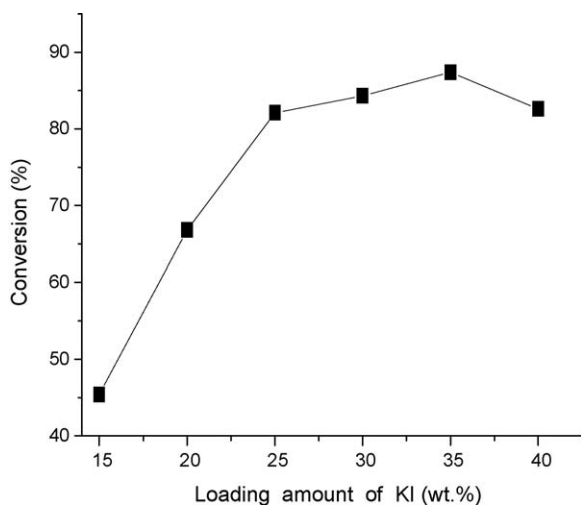


Fig. 7. Influence of loading amount of KI on the conversion. Reaction conditions: methanol/oil molar ratio, 15:1; catalyst amount, 2 wt.%; reaction time, 6 h; methanol reflux temperature.

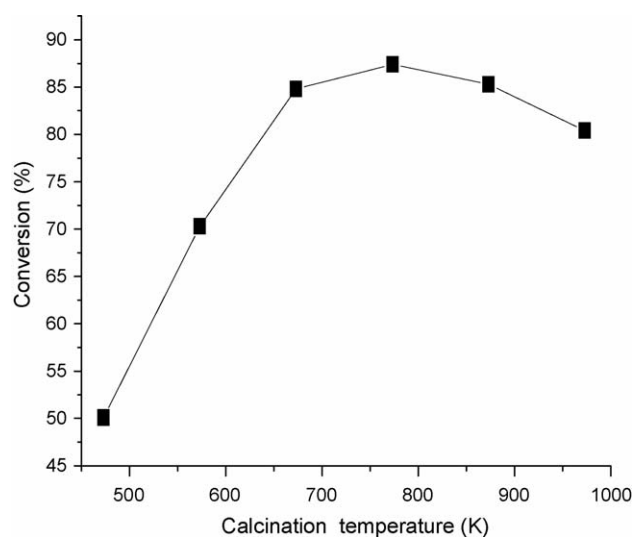


Fig. 8. Influence of calcination temperature on the conversion. Reaction conditions: methanol/oil molar ratio, 15:1; catalyst amount, 2 wt.%; reaction time, 6 h; methanol reflux temperature.

was obtained at loading KI of 35 wt.% on Al₂O₃. However, when the amount of loaded KI was over 35 wt.%, the conversion was decreased, most likely owing to that the excess KI could cover the basic sites on the surface of the composites and cause a lowered catalytic activity. On the basis of the results, the optimum-loading amount of KI was 35 wt.%. More significantly, in view of Figs. 1 and 7, it is obvious that the change in the activity of the catalysts was well correlated to the change of their basicity, indicating that the activity of the catalysts is dependent on their basicity if the base strengths remain constant.

The catalytic activity of 35 wt.% KI/Al₂O₃ sample for this reaction is plotted as a function of calcination temperature in Fig. 8. Clearly, the activity change profiles indicated that the catalytic activities of the composites strongly depended on the calcination temperature. In the absence of calcination, the KI/Al₂O₃ sample as prepared did not display any particular catalytic activity, as expected, due to the lack of strong basic sites on which transesterification reaction could occur. After calcination at elevated temperatures, however, the catalysts exhibited a higher catalytic activity. Such a result suggested that the high-temperature pretreatment was indispensable for getting high activities of the catalysts. Moreover, as shown in Fig. 8, the conversion to methyl esters was gradually increased with the rise of the calcination temperature from 473 to 773 K, which could be correlated well with the increase of the catalyst basicity with the increase of the calcination temperature between 473 and 773 K (Fig. 2). However, when the calcination temperature was higher than 773 K, the conversion dropped considerably resulting from a lower basicity. The optimal calcination temperature was 773 K. When calcined at 773 K, the catalyst exhibited the highest basicity and, therefore the highest catalytic activity for the transesterification reaction, giving a maximum conversion of 87.4%. Since KI is inactive for this reaction, the activity variation of the catalysts calcined at different temperatures should be attributed to the different KI decomposition extents and distribution of potassium on the alumina support. Thus, the decrease

in catalytic activity at a higher temperature, probably, results from the loss of potassium species by sublimation or penetration into the subsurface. Notably, by comparing Figs. 2 and 8, it was found that the activity of the catalysts could be also correlated to their basicity as mentioned above, further demonstrating that the higher basicity could result in the higher conversion.

Undoubtedly, the activity of the $\text{KI}/\text{Al}_2\text{O}_3$ catalyst is dependent not only upon the strength of basic sites but also upon their amount. The more the amount of the basic sites, the higher the activity of the catalyst. The basic sites are proportional to the decomposed amount of KI, instead of the loaded amount of KI. The decomposition products of KI, probably forming both K_2O species and Al–O–K groups in the composite, were possibly the main active sites for the transesterification reaction. However, there was poor direct experimental evidence for the existence of K_2O species and Al–O–K groups in framework of the composite, and therefore, the investigation on further aspects of the catalyst, practically on the catalytically active sites and the recyclability of catalysts, is needed.

3.5. Influence of the reaction conditions

The transesterification process consists of a sequence of three consecutive reversible reactions where the triglyceride is successively transformed into diglyceride, monoglyceride, and finally into glycerin and the fatty acid methyl esters. The molar ratio of methanol to soybean oil is one of the important factors that affect the conversion to methyl esters. Stoichiometrically, three moles of methanol are required for each mole of triglyceride, but in practice a higher molar ratio is employed in order to drive the reaction towards completion and produce more methyl esters as products. Fig. 9 reflects the effect of methanol/oil molar ratios on the conversion. As shown in this figure, with an increase in the methanol-loading amount, the conversion was increased considerably. The maximum conversion was obtained when the molar ratio was very close to 15:1. However, beyond the molar ratio of

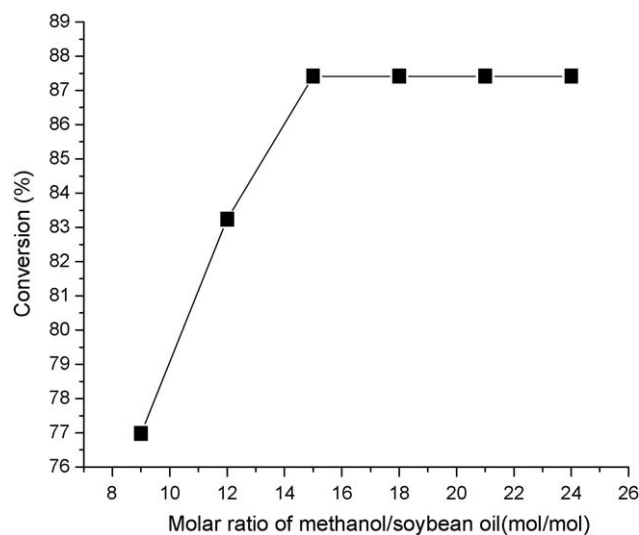


Fig. 9. Conversion of soybean oil as a function of methanol/oil molar ratio. Reaction conditions: catalyst amount, 2 wt.%; reaction time, 6 h; methanol reflux temperature.

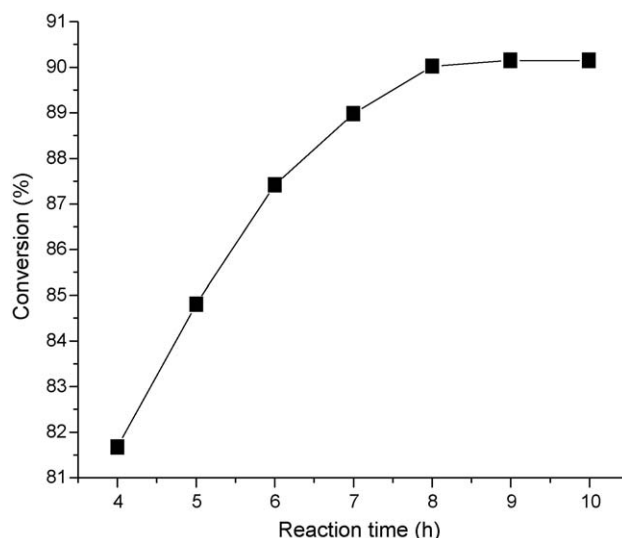


Fig. 10. Conversion of soybean oil as a function of reaction time. Reaction conditions: methanol/oil molar ratio, 15:1; catalyst amount, 2 wt.%; methanol reflux temperature.

15:1, the excessively added methanol had no significant effect on the conversion. Therefore, the optimum molar ratio of methanol to soybean oil to produce methyl esters was approximately 15:1.

The dependence of the conversion to methyl esters on the reaction time was studied in the presence of 35 wt.% $\text{KI}/\text{Al}_2\text{O}_3$ catalyst at reflux of methanol. The reaction time was varied in the range 1–10 h. As can be seen from Fig. 10, the conversion was increased steadily in the reaction time range between 4 and 8 h, and thereafter remained nearly constant as a result of a nearly equilibrium conversion; the maximum conversion of soybean oil was achieved after 8 h.

The influence of the catalyst amounts was studied at a 15:1 molar ratio of methanol to soybean oil at reflux of methanol for 8 h. The catalyst amount was varied in the range of 1.0–3.5%. These percentages were weight fractions of the oil supplied

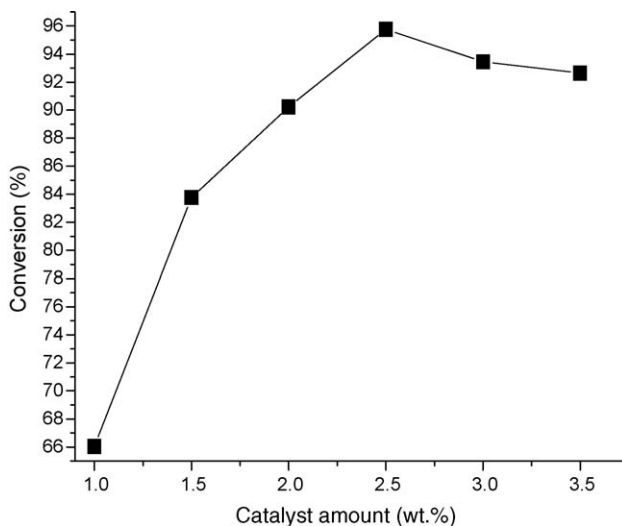


Fig. 11. Conversion of soybean oil as a function of catalyst amount. Reaction conditions: methanol/oil molar ratio, 15:1; reaction time, 8 h; methanol reflux temperature.

for this reaction. The reaction profile of Fig. 11 indicated that the transesterification reaction was strongly dependent upon the catalyst applied. Without addition of a catalyst, the transesterification did not occur, while the presence of the supported catalyst significantly increased the reaction rate. As is evident from Fig. 11, when the catalyst amount increased from 1% to 2.5%, the conversion to methyl esters was increased. However, with further increase in the catalyst amount the conversion was decreased, which was possibly due to a mixing problem involving reactants, products and solid catalyst. At about 2.5% catalyst amount, a high conversion of up to 96% was obtained.

4. Conclusions

Alumina loaded with potassium iodide, which was prepared by impregnation of powdered alumina with an aqueous solution of KI followed by calcination at a high temperature in air, showed high catalytic activities for the transesterification reaction. Both the K_2O species formed by the thermal decomposition of loaded KI, and the surface Al–O–K groups formed by salt–support interactions, were probably the main reasons for the catalytic activity towards the reaction. The activities of the heterogeneous base catalysts correlated with their corresponding basic properties. The catalyst with 35 wt.% KI loading on Al_2O_3 and calcined at 773 K for 3 h was found to be the optimum catalyst, which gave the highest basicity and the best catalytic activity. When the reaction was carried out at reflux of methanol, with a molar ratio of methanol to oil of 15:1, a reaction time 8 h, and a catalyst amount 2.5%, the highest conversion of soybean oil reached 96%.

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