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Article

Aspects of stability of K/Al₂O₃ catalysts for the transesterification of rapeseed oil in batch and fixed-bed reactors

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ABSTRACT

Catalytically active, stable, and mechanically durable solid K/Al₂O₃ catalysts for the transesterification of rapeseed oil with methanol was studied. In a batch reactor, high catalytic activity was accompanied by leaching of K species, caused by glycerol, and mechanical destruction of the solid catalyst as a result of contact with the stirrer. In a fixed-bed reactor, some leaching of K species into the liquid phases was also observed, but approached 0 during 30 h of time-on-stream; the activity of the K/Al₂O₃ catalyst (~83% ester yield) was stable for 100 h of time-on-stream and no mechanical destruction of the catalyst was observed. The populations of K₂O and K-O-Al species for fresh and used K/Al₂O₃ catalysts were compared using Fourier transform infrared spectroscopy. It was found that some K₂O species leached into the liquid phases at the beginning of the reaction.

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1. Introduction

Biodiesel is a renewable fuel for use in diesel engines, and it is receiving increasing attention, mainly because of its environmentally friendly properties [1]. Biodiesel is produced commercially by the homogeneous transesterification of vegetable oils with methanol using KOH as a catalyst. Homogeneous base catalysts exhibit high catalytic activity, but a large amount of water is required to remove the residual homogeneous catalyst, and it is impossible to reuse homogeneous catalysts [2]. Heterogeneous catalysts are attractive because the catalytic system can be separated and reused [3–5]. However, the catalytic activity of heterogeneous catalysts for transesterification is lower than that of homogeneous catalysts, and leaching of active species into the liquid products is possible.

Supported alkali metal hydroxides or salts are among the most-studied solid heterogeneous catalytic systems for the

transesterification of vegetable oils [6]. Supported K-based catalysts, particularly Al₂O₃-supported catalysts, are attractive because of their high basicity and relatively easy and cheap synthesis. Several authors have described solid K-based catalysts with high catalytic activity; for example, ester yields greater than 90% using K₂CO₃/Al₂O₃ [7,8], KF/Al₂O₃ [9,10], KOH/Al₂O₃ [11,12], and KNO₃/Al₂O₃ catalysts [13,14] have been reported. However, the main problem in applications of these catalysts is their stability.

Most authors reported continuous drops in the activity of KNO₃/Al₂O₃ [14], KF/Al₂O₃ [10,15], K₂CO₃/Al₂O₃ [8,16,17], and KOH/Al₂O₃ catalysts [12,18] after the first catalytic cycle. Catalyst deactivation was explained by the leaching of K into the liquid phases. The reason for this is still under discussion. It has been explained by attack of K by methanol [8,16,18] and glycerol [10,19] or by covering of the catalyst surface by glycerol [10].

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Isahak et al. [11] and Verziu et al. [20] reported stable activity of KOH/Al₂O₃ and KF/Al₂O₃, respectively, over four cycles in catalytic tests (95%–85% ester yields). However, significant decreases in the performance of KOH/Al₂O₃ and KF/Al₂O₃ catalysts were observed in cycles five (~70% ester yield) and six (~30% ester yield). The decrease in catalytic activity was associated with K leaching. Wen et al. [21] reported a biodiesel yield exceeding 91% even after 16 catalytic cycles. However, the concentration of K in the solid catalyst or in the liquid phases during the 16 catalytic cycles was not reported.

As discussed above, solid K-based catalysts have mainly been studied using batch reactors. Although there have only been a few studies focusing on the use of fixed-bed reactors with this type of catalyst in the transesterification of rapeseed oil, fixed-bed reactors have many advantages such as the absence of other catalyst separation and continual product formation. For example, Furuta et al. [22] reported ester yields of more than 90% using W-ZrO₂/Al₂O₃ for up to 100 h of time-on-stream, with the reaction temperature kept at 250 °C.

Previously, we focused on the leaching of K species from solid K/Al₂O₃ catalysts into the liquid phases during transesterification [19]. It was found that K species were leached into the liquid phases as a result of attack by produced glycerol. The aim of this work is to study the catalytic behaviours of K/Al₂O₃ catalysts in batch and fixed-bed reactors. Attention is also focused on the stability of K₂O and K–O–Al species in the reaction.

2. Experimental

2.1. Catalyst preparation

An alumina support with a particle diameter of 3–5 mm was supplied by Euro Support Manufacturing Czechia. The K/Al₂O₃ catalyst (16.1 wt% K) was prepared by the wet impregnation method. A mixture of the support in an aqueous solution of KOH (90% purity, Lachner, Czech Republic) was stirred at 95 °C for 4 h. Excess water was removed at the same temperature until dryness. The K/Al₂O₃ catalyst was then dried for 24 h at room temperature. Finally, the catalyst was calcined in an air flow at 475 °C for 4 h.

2.2. Catalyst characterization

Fourier transform infrared (FT-IR) spectra of the samples were obtained on Nicolet 6700 FT-IR spectrometer using KBr pellets, with accumulation of 64 scans at a spectral resolution of 4 cm⁻¹. The scanning range was from 400 to 4000 cm⁻¹. All measurements were conducted at room temperature.

2.3. Catalytic tests and product analysis

2.3.1. Batch reactor

The reactions were carried out in a stainless-steel batch reactor (150 mL). Rapeseed oil (cold-pressed, filtered, free of erucic acid, acid number 1.2 mg KOH/g, water content 610 mg/kg, density 920 kg/m³ at 25 °C, kinematic viscosity 35.0 mm²/s at 40 °C; RPN Slatiňany) and methanol (p.a., 0.04% wa-

ter content, determined using the Karl Fischer method) were used. Oil (50 g), methanol (methanol to oil molar ratio 24:1), and the catalyst (4 wt% of catalyst based on the mass of rapeseed oil) were put in the reactor and heated to the reaction temperature (117 °C). The stirring rate was 320 r/min. After reaction (8 h), the catalyst was filtered off and the methanol was removed from the reaction mixture by evaporation (2 kPa and 65 °C). The ester phase (upper phase) and glycerol phase (lower phase) were separated in a separating funnel and analysed. The reusability of the catalyst was checked over five consecutive cycles under the reaction conditions described above. No further purification of the catalyst was performed between each cycle. Additionally, the catalyst was placed in contact with pure glycerol after five consecutive catalytic cycles (1g of catalyst and 5.2 g of glycerol were used, the total K leaching was calculated based on the amount of K in the fresh catalyst).

2.3.2. Glycerol washing in batch reactor

The resistance of the K/Al₂O₃ catalyst to glycerol was checked over five consecutive cycles in the presence of glycerol. Pure glycerol was used in each cycle and the catalyst was not purified between cycles. The tests were performed by washing 3 and 6 g of K/Al₂O₃ catalyst with 15.6 and 31.2 g of pure glycerol, respectively. The amount of glycerol used was calculated based on the theoretical value for total oil conversion: 5.2 g of glycerol is produced if 50 g of oil and 1 g of catalyst are used. Reaction conditions: 65 °C, 320 r/min, and 7.5 h.

Catalytic test was performed after five consecutive washing cycles with glycerol under the same reaction conditions (batch reactor, rapeseed oil 50 g, 2 g of catalyst, 117 °C, 8 h, 320 r/min, methanol:oil = 24:1).

2.3.3. Fixed-bed reactor

Catalytic tests were performed using a bench-scale catalytic apparatus equipped with an electrically heated fixed-bed reactor of inner diameter 17 mm. Food-grade rapeseed oil and methanol were used as liquid feeds. Prior to the catalytic tests, the catalyst (10 g) was diluted with silicon carbide (1.2 mm diameter; the catalyst:SiC volume ratio was set to keep the total volume of catalyst plus SiC constant; constant catalyst bed height). Once the reaction temperature of 115 °C was reached in the reactor (the temperature gradient was set at 40 °C/h), the catalyst was dried for 4 h under N₂ (4 MPa, 10 NL/h). Transesterification of the rapeseed oil was studied under the same N₂ pressure and at 115 °C. The mass hourly space velocity (WHSV) was set at 1.43 g/(g·h) and the methanol:oil molar ratio was 12:1. After the reaction, the methanol was removed from the reaction mixture by evaporation (2.3 kPa and 65 °C) and the ester and glycerol phases were separated in a separating funnel and analysed.

2.3.4. Ester phase analysis

The ester phase was analysed by GC, according to EN 14105, using a Shimadzu GC-2010 instrument, and linear calibration curves of pure methyl esters. Methyl esters were identified in the chromatogram; calibration standards were prepared by

homogeneous transesterification of the same oil and purification by molecular distillation. The ester yield (Y_E) was calculated according to eq. (1).

$$Y_E (\%) = \frac{m_E}{m_O} \cdot 100 \quad (1)$$

where m_E is the mass of methyl esters and m_O is the amount of oil fed into the reaction.

2.3.5. Glycerol phase analysis

The amount of glycerol in the glycerol phase, if formed, was determined by iodometric titration and the concentration of K was determined.

2.3.6. K leaching

The concentration of K ions in each phase was determined using flame photometry (Flame photometer 410, Sherwood), using linear calibration curves. The calibration solutions for K determination in the ester phase were prepared by mixing a methanolic KOH solution (close to saturation) with a biodiesel matrix without any ions [23]. The biodiesel matrix was prepared by washing the biodiesel with an aqueous solution of citric acid. The concentration of K ions in the ester phase was directly determined. Aqueous solutions of KOH were used as calibration standards for the determination of K ions in the glycerol phase. A sample of the glycerol phase was diluted with water and the K ion concentration was determined. The influence of glycerol on the K determination can be neglected in this case, because highly dilute glycerol samples were used.

3. Results and discussion

3.1. Batch reactor

Table 1A shows the activity of the 16.1 wt% K/Al₂O₃ cata-

leached into glycerol was the same at different absolute amounts of $\text{K}/\text{Al}_2\text{O}_3$ catalyst. Comparable results obtained from several tests support this finding. It should also be mentioned that partial disintegration of the $\text{K}/\text{Al}_2\text{O}_3$ catalyst grains was observed after five washing cycles (Fig. 3(c)).

In our previous work, leaching of K species into methanol, oil, and esters was not observed under the same conditions as those used with glycerol [19].

3.3. Role of glycerol in K leaching

The information on the amount of K leaching from the catalyst is very important. In the batch reactor, 66% and 65% of K were leached into glycerol from the catalyst over five consecutive washing cycles (Fig. 1). In the fixed-bed reactor, 60% of K was leached from the catalyst during reaction for 100 h of time-on-stream (Fig. 2).

Finally, 51% of K (Table 1A) was leached from the catalyst over five consecutive catalytic cycles in the batch reactor (42%) followed by washing with glycerol (9%).

Although K leaching into methanol [8,16,18] and glycerol [10,19] has been observed, no K in the second to fifth catalytic cycles was lost, i.e. when no glycerol phase was formed but methanol was present in the reaction mixture. However, another 9% of K was leached from the used catalyst (after five consecutive catalytic cycles, shown in Table 1A) into glycerol. The leaching of K from the used catalyst after five consecutive catalytic tests into glycerol shows that the glycerol phase plays a critical role in K leaching. The reason for the lower amount of leached K after five consecutive catalytic tests in the batch reactor followed by washing of the used catalyst in glycerol (51%) is probably the absence of other washing cycles of the catalyst in glycerol (Table 1A); the loss was caused by mechanical damage to the catalyst (similar to Fig. 3(d)).

The decrease in the stability of the K/Al₂O₃ catalyst between the first and second catalytic cycles is in agreement with most reports on the stability of K-based catalysts in transesterification of rapeseed oil [12,16–18,24].

The results reported here support the proposal that K species are leached from the K/Al₂O₃ catalyst by the attack of glycerol [10,19] and not methanol [8,16,18]. Moreover, the fact that K species are leached only if the glycerol phase is separated from the ester phase could be the reason for the discrepancies in the stability of K-based catalysts reported in the literature. Possible K leaching and its detailed analysis were not described by Wen et al. [21]; they reported biodiesel yields exceeding 91% even after 16 catalytic cycles. Decreases in the activity of K-based catalysts after the fifth and sixth consecutive cycles were reported by Isahak et al. [11] and Verziu et al. [20], respectively. Although K leaching was reported as the reason for deactivation, a detailed analysis of K in the glycerol and ester phases was not provided.

3.4. Stability of K/Al₂O₃ catalyst

The stable activity of the K/Al₂O₃ catalyst in the fixed-bed reactor for 100 h shows that the residual K species present in the catalyst have high activity in transesterification. This is probably the reason for the very high activity of a K/CaO catalyst after 16 consecutive catalytic tests reported by Wen et al. [21]. However, this could not be proved because an analysis of the K present in the solid catalyst and/or liquid phases is not given in that paper. Our results for 100 h of time testing of the catalytic activity and stability are comparable to, or higher than, the average results reported in the literature. For example, Di Serio et al. [25] and Sankaranarayanan et al. [26] tested the

activity and stability of Mg-Al mixed oxide and MoO₃ supported on Al₂O₃ in transesterifications for 80 and 120 h, respectively. The MoO₃/Al₂O₃ catalyst had long-term stability (conversion dropped only about 5% during the catalytic tests and 1% of MoO₃ was leached) [26], but the Mg-Al mixed oxide catalyst was deactivated rapidly in the first hour on stream [25]. However, it was possible to regenerate the catalyst by simply washing with acetone [25]. Continuous testing for about 8 h was reported by Sherstyuk et al. [27]. It was found that the rapeseed oil conversion remained nearly constant during the tests with some binary catalytic systems. Melero et al. [28] tested the activity and resistance against deactivation of Zr-SBA-15/bentonite catalyst for more than 260 h of time-on-stream in transesterifications, and obtained promising results (the catalytic activity remained practically the same during the entire test and the physicochemical properties of the catalyst were similar before and after use). However, tests under flow conditions of a comparable catalytic system to that studied in this work have not yet been reported; therefore, it is hard to compare the reported results with those in this work.

The use of a fixed-bed reactor is favourable in heterogeneous catalysis. Other studies of the use of K catalysts in flow-type reactor have been reported. Buasri et al. [29] tested KOH supported on coconut-shell activated carbon in a packed-bed reactor for the transesterification of waste frying oil; there was no evidence of catalyst deactivation. However, the leaching of active species was not discussed. Furuta et al. [30] studied K/ZrO₂ in the transesterification of soybean oil using a fixed-bed reactor. This catalyst gave almost 100% oil conversion at the beginning of the reaction, but it was deactivated rapidly due to K leaching from the catalyst.

In the case of the K/Al₂O₃ catalyst, the high and stable activity, even when some K leaching occurs at the beginning of the reaction, and the absence of mechanical destruction, show its high potential for use in transesterification. The main aim in the future will be to fix all the K on the support under the reaction conditions.

3.5. Stability of individual K species

FT-IR spectroscopy was used to investigate the stability of K species in the K/Al₂O₃ catalysts. Figure 4 shows the spectra of the fresh and used catalysts after five consecutive cycles in the batch reactor and after 130 h of time-on-stream. All the samples showed a very intense broad band at around 3400 cm⁻¹, which could be assigned to the O–H stretching vibration of the hydroxyl groups attached to Al₂O₃. This band could also be partly attributed to the stretching vibrations of Al–O–K groups [31,32]. The minor absorption peak at about 1640 cm⁻¹ may be assigned to the O–H bending vibration mode of H₂O molecules adsorbed from air [13]. In addition, there were two bands at around 1540 and 1400 cm⁻¹, which were attributed to the vibrations of CO₃²⁻ ions; the adsorption of gaseous CO₂ from the ambient atmosphere on the basic sites of K₂O may account for the presence of carbonates [33,34]. The band at 585 cm⁻¹ (AlO₆ groups) and the weak band at 792 cm⁻¹ (AlO₄ groups) were attributed to aluminate bands, and indicate the presence of

Al-O-Al framework [31,35].

The intensity of the bands at 1540 and 1400 cm^{-1} attributed to K_2O species for the $\text{K}/\text{Al}_2\text{O}_3$ catalyst after five consecutive cycles in the batch reactor and after 130 h of time-on-stream in the fixed-bed reactor decreased significantly compared with that of the fresh catalyst. In contrast, the intensity of the band at 3400 cm^{-1} partly reflected to the Al-O-K groups only decreased slightly compared with that of the fresh catalyst. It was therefore concluded that some K_2O species were leached out of the catalyst during the reaction. This observation is in agreement with the previously reported suggestion that K_2O species are leached from solid K-based catalysts into the liquid phase [33].

We previously reported that the leaching of K species was caused by the attack with the formed glycerol [10,19], and not

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