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Transesterification of triacetin with methanol on various solid acid catalysts: A role of catalyst properties

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ABSTRACT

Present studies concentrated on a comparison of catalytic performance of number of solid acid catalysts, namely Amberlyst-15, Nafion-SAC-13, polyaniline-sulfate, silver and cesium salts of $H_3PW_{12}O_{40}$ in transesterifiaction of triglycerides with methanol. Reaction was studied for triacetin, the short triglyceride and for castor oil consisting of vegetable fatty acid esters under mild reaction conditions (atmospheric pressure, 50 °C). The catalysts were characterized by measuring textural (specific surface area, porosity, pore diameter) and acid (concentration and the strength of acid centers) properties. The affinity of catalyst to highly hydrophobic triglyceride reactant relative to that toward rather hydrophilic glycerol was also evaluated from the measurements of contact angles for droplets of triacetin, castor oil and glycerol on the surface of pressed tablet of catalyst. This affinity of catalysts was also evaluated from the drop of catalyst activity induced by glycerol added to the reaction mixture or by pre-treatment of catalyst with triacetin. $Cs_2HPW_{12}O_{40}$ salt was the most active catalyst, but it deactivated in the transesterification. The highest strength of acid sites and high affinity to glycerol was determined for this Cs salt. Thus, affinity of studied catalysts toward glycerol and the strength of acid sites seem to be decisive factors for their activity and in particular for deactivation due to polar reagents adsorption. Greater affinity toward glycerol and higher strength of acid sites, deactivation of catalysts would be easier.

1. Introduction

Biodiesel fuel, an alternative to classic diesel fuel, belongs to ecological fuels because it consists of methyl esters of fatty acids, derived from vegetable oils or animal fats. Methyl esters are obtained by the transesterification of triglycerides with short-chain alcohols, such as methanol. The reaction is catalysed by strong acids or bases, but owing to environmental, technological, and economic reasons, the substitution of industrial homogeneous catalysts by heterogeneous catalysts is a desirable goal.

The advantage of solid catalysts consists in the ease of product separation and recycling of the catalyst. Furthermore, solid catalysts can be used in a packed bed continuous flow reactor, simplifying the product separation and purification. Moreover, solid acid catalysts are preferred because they are able to catalyse both transesterification of triglycerides and esterification of free fatty acids present in oil feedstock. A variety of solid acids has already been tested for methyl ester synthesis via both, esterification of free fatty acid and transesterification of triglycerides. Their catalytic efficiency has been reviewed in recently published papers [1–5]. Among heterogeneous acid catalysts the samples based on inorganic oxides namely sulfated zirconia [6–9], tungstated zirconia [8,10,11], strong mineral acids such as Keggin type heteropolyacid $H_3PW_{12}O_{40}$ supported by zirconia, silica, alumina, activated carbon [12] and Ta_2O_5 [13] and its cesium salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [14] were mainly studied. Recently, a new class of sulfonated carbons catalysts, termed as “sugar catalysts” was reported. They were prepared by incomplete carbonization of simple carbohydrates (starch, cellulose, glucose, sucrose) followed by sulfonation [15,16]. Sulfonic acids – based ion-exchange resins are another class of solid acid catalysts known to be effective in the formation of methyl esters via esterification and transesterification reactions. They are styrene-based sulfonic acid, Amberlyst-series, and perfluorosulfonic acid-based resins, Nafion and Nafion SAC-13 composite [5,17,18], (polystyrene-divinylbenzene)-based sulfonic acid [19], sulfonated poly(styrene-co-divinylbenzene) and sulfonated poly(divinylbenzene) [20].

Some common problems encountered for solid acid catalysts concern appropriate morphological, textural and acid characteristic of the samples. Apart from them, hydrophilic character of catalyst surfaces and active site leaching resulting in deactivation

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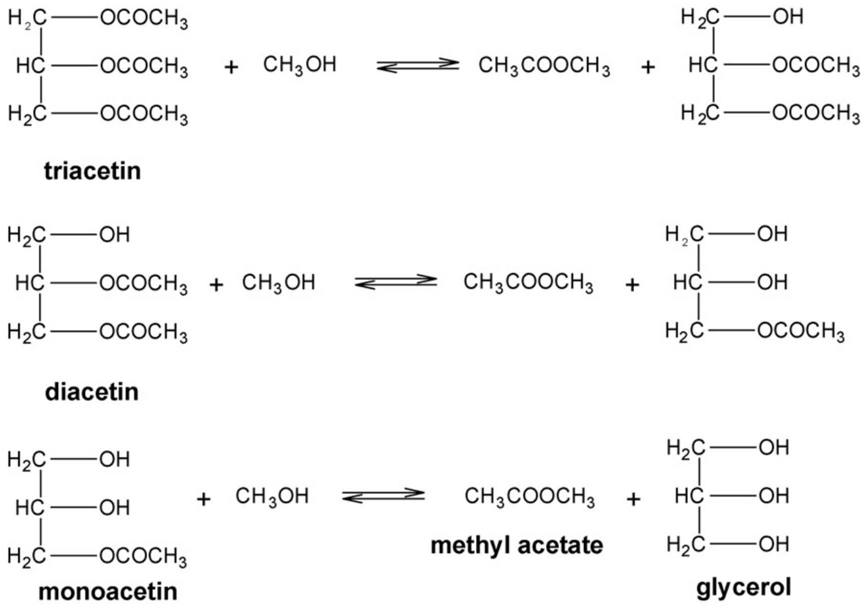

Scheme 1. Transesterification of triacetin with methanol.

of catalysts are frequently discussed. Other reason of catalyst deactivation is partial blockage of acid centers due to accumulation of polar reagents like glycerol and/or partial glycerides (di- and mono-) inside pore structure of catalysts [5,21]. Thus, to avoid polar reagents accumulation, appropriate textural/morphological characteristics and hydrophobic nature of catalyst surface to promote the preferential adsorption of triglycerides are needed. This was achieved by incorporation of hydrophobic organic groups (alkyl and phenyl) into mesoporous silica materials. More hydrophobic environment around active centres was created in which water molecules, product of fatty acids esterification were easier excluded from the mesopores enhancing the activity of catalysts [21]. Similar strategy of tuning hydrophobic/hydrophilic balance of the catalysts was also successfully adopted in case of catalysts for transesterification of triglycerides [22,23]. It was demonstrated that modification of support with alkyl or phenyl groups in hybrid catalyst $Ta_2O_5/SiO_2–[H_3PW_{12}O_{40}/R]$ R = Me, Ph, resulted in higher activity and much lower deactivation for simultaneous esterification and transesterification of soybean oil with methanol compared to alkyl-free HPW/Ta_2O_5 catalyst [13,22]. Similar effect was obtained by incorporation of organosulfonic groups into mesostructured silica SBA-15 [23,24]. In esterification of free fatty acids present in beef tallow the propylsulfonic acid-functionalized SBA-15 catalyst deactivated due to the condensation of reagents in the mesopores of catalysts. This was explained by too high polarity of the catalyst. Bifunctionalization of the SBA-silica support via simultaneous incorporation of propylsulfonic groups and propyl groups resulted in enhanced hydrophobicity of the catalyst thereby diminishing the interaction of the polar molecules with the sulfonic acid groups, a reason of catalyst deactivation. Very promising performance of propylsulfonic acid-modified SBA-15 catalyst towards simultaneous esterification of fatty acids and transesterification of triglycerides using refined and crude vegetable oils was demonstrated by Melero et al. [24].

In view of these literature observations, relative affinity of catalyst to non-polar triglyceride and more polar intermediates (diglyceride, monoglyceride) and products, glycerol is an important property. Weak adsorption of glycerol molecules and strong adsorption of triglyceride molecules are preferred. However, it can be expected that these adsorption properties would be to some extent determined by the strength of acid sites in the catalyst. This effect is studied and discussed in the present work using various solid acid catalysts. Polymeric catalysts Amberlyst-15, Nafion-SAC-13, polyaniline-sulfate (PANI-S) and cesium and silver salts of Keggin type heteropolyacid, $H_3PW_{12}O_{40}$ (HPW), namely $Cs_2HPW_{12}O_{40}$ (abbreviated as Cs-2), $Cs_{2.5}H_{0.5}$ $PW_{12}O_{40}$ (abbreviated as Cs-2.5) and $Ag_2HPW_{12}O_{40}$ (abbreviated as Ag-2) were tested.

Commercial resins, Amberlyst-15 and Nafion-SAC-13 are well known to be effective solid acid catalysts in esterification of fatty acids and transesterification of triglycerides. Polyaniline salts, a hydrochloride, sulfate, nitrate, p-toluenesulfonate and phosphate, have been studied by Palaniappan et al. [25,26] as the solid acid catalysts for various organic transformations, among them for the esterification of carboxylic acids with alcohols. Polyaniline-sulfate (PANI-S) was also studied for the transesterification of triglycerides in our previous work [27]. The activity of PANI-S was found to be almost stable during recycling catalytic tests in esterification as well as transesterification reactions [26,27]. Among $Cs_xH_{3-x}PW_{12}O_{40}$ salts of various Cs content ranging from $x = 1$ up to $x = 3$, the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt is known to be the most active acid catalyst for various reactions, performed in gas-phase like isomerization, alkylation, dehydratation [28,29]. This excellent activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was related to its superacidity, high surface area and mesoporous structure [30]. This salt was also most active than H-ZSM-5, $SiO_2–Al_2O_3$, $SO_4{}^{2-}/ZrO_2$, Nb_2O_5 in liquid phase reactions, such as hydrolysis of ethyl acetate and 2-methylphenyl acetate, esterification of acrylic acid with n-butanol [30]. $Cs_2HPW_{12}O_{40}$ salt exhibits also strong acid centres, however due to very low surface area (ca. 1 m^2/g) and microporous structure its activity in gas phase reaction was very low, distinctly lower than that of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Both such salts were shown to be active catalysts for transesterification of triglycerides [31,32] however, another order of activity was observed. In methanolysis of tributyrin and esterification of palmitic acid Narasimharao et al. [30] observed that Cs salts with Cs content $x = 2–2.3$ were much more active than Cs-2.5. Analogous relation was also obtained in our previous studies [32]. The activity of Cs-2 was higher than that of Cs-2.5 in methanolysis of triacetin and castor oil. This relation was explained taking into account that the salt of HPW, such as Cs, Ag and K formed colloidal dispersion in reaction medium during transesterification of triglycerides, mostly due to the presence of methanol. Due to open pore structure of colloidal particles, the role of specific surface area and porosity determined for solid-powdered samples was less important. Colloidal particles facilitated the access of reagents to protons of the salts and activity was related to the bulk (formal) acidity of the Cs salts similarly to the relation reported by Izumi et al. [33] for the hydrolysis of ethyl acetate under excess of water. Under these conditions their activity decreased monotonously with increasing Cs content or decreasing acidity. In our previous work, silver salts, namely $Ag_2HPW_{12}O_{40}$ and $Ag_{2.5}H_{0.5}PW_{12}O_{40}$ were also tested for methanolysis of triglycerides [34]. They also formed colloidal particles in reaction mixture and Ag-2 salt was more active than Ag-2.5. The catalysts Amberlyst-15, Nafion-SAC-13, polyaniline-sulfate, Ag-2, Cs-2 and Cs-2.5 tested in the present work displayed good stability under methanolysis reactions owing to high resistant for active sites leaching [26,27,31].

Here, methanolysis was studied for triacetin (glycerol triacetate), a model triglyceride molecule and for vegetable oil, castor oil. The methanolysis of triacetin (the acetic acid triester of glycerol) which is the simplest triglyceride has already been studied as a model reaction for the transesterification of natural oils [18,35–39]. Triacetin, having the same chemical functionality of any triglyceride molecule, shares the same reactivity principles of triglycerides and its methanolysis is accomplished via three sequential steps, similarly to the methanolysis of other triglycerides. Reaction pattern reported by Lopez et al. [35] (Scheme 1) shown that methanolysis proceeds via the intermediate products, diacetin and monoacetin to produce finally methyl acetate and glycerol. Castor oil derived from *Riccinus communis* plants is mentioned frequently in the literature as a potential raw material for biodiesel and its transesterification was studied by Plentz Meneghetti et al. [40,41]. The main constituent of castor oil is triglyceride of 12-hydroxy-9-octadecenoic acid (ricinoleic acid). Due to the presence of OH group at C-12 carbon, the castor oil exhibits good solubility in methanol and it applies also to methyl esters formed after its transesterification. Similarly, triacetin is also readily soluble in methanol and methyl esters formed. Thus, during methanolysis of both our triglycerides, there was a single liquid-phase system. Moreover, by using a triacetin, the model compound, we are able to gain some insight into the role of catalyst properties in the course of consecutive reactions yielding partial glycerides, diacetin and monoacetin.

It should be pointed out that all catalysts selected for the present work have been previously studied for the transesterification of triglycerides. Literature data and in particular the results of Dr. Goodwin group proved no leaching of active centers in case of polymeric catalysts, Nafion-SAC-13 and Amberlyst-15 [18,35]. In recycling methanolysis experiments they slowly deactivated, however due to partial blockage of active sites by reagents. The heterogeneous mode of HPW salts was also proved by results of Narasimharao et al. [31] and Chai [14]. The stability of polyaniline-sulfate catalysts was demonstrated by Palaniappan et al. [25,26] in various esterification reactions and in our earlier work in the transesterification of triacetin and castor oil [27].

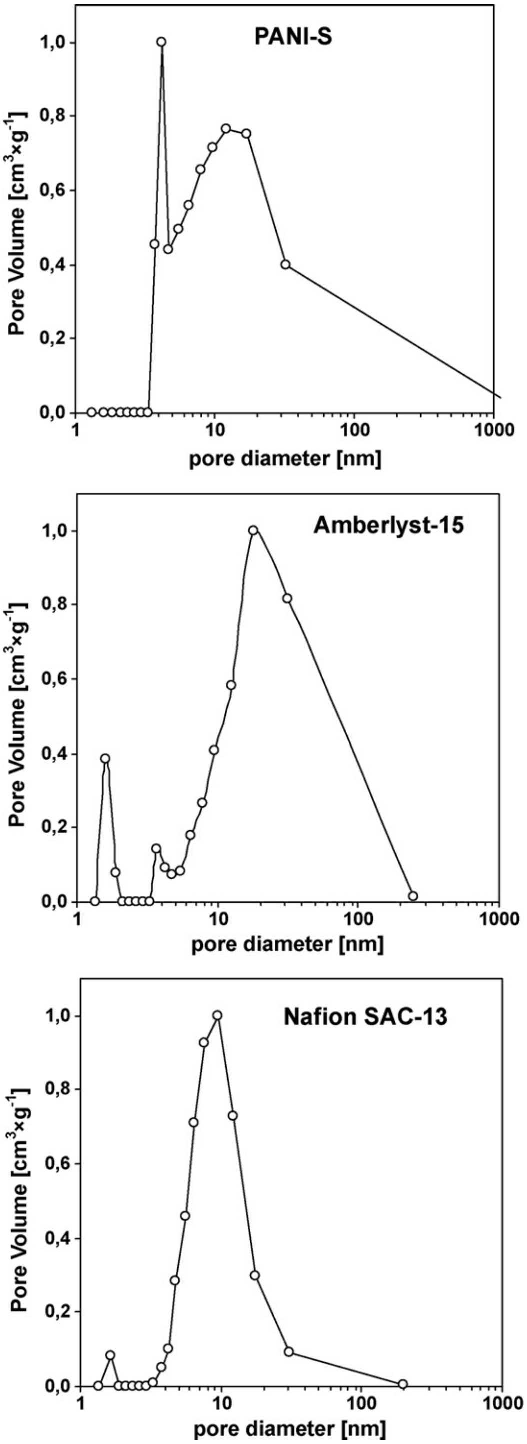

Fig. 1. Pores distribution diagrams for polymeric catalysts PANI-S, Amberlyst-15, Nafion-SAC-13.

2. Experimental

2.1. Catalysts preparation

Amberlyst-15 and Nafion-SAC-13 were commercial reagents (Aldrich). Polyaniline sulfate (PANI-S) powder was prepared by the oxidation of 0.1 M aniline sulfate with 0.25 ammonium peroxydisulfate in 50 vol.% ethanol–water at room temperature. The solids were collected after 24 h on filter, rinsed with 0.1 M sulfuric acid, acetone, and dried. The details of preparation were described in our previous paper [27].

The cesium and silver salts of $H_3PW_{12}O_{40}$, namely $Cs_2HPW_{12}O_{40}$ (Cs-2), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs-2.5) and $Ag_2HPW_{12}O_{40}$ (Ag-2) were prepared by means of commonly used procedure [42]. The stoichiometric quantities of cesium carbonate, or silver nitrate were added to aqueous solutions of the 12-tungstophosphoric acid (Aldrich). The concentrations of HPW and cesium/silver salt solutions were 0.10 and 0.04 M, respectively. The Cs or Ag content (x) in final salts was adjusted by the amount of precipitating solutions (Cs_2CO_3 or $AgNO_3$) added. The preparation was performed at ambient temperature without stirring. The resulting white colloidal solution of

Cs, Ag salts was slowly evaporated overnight in the oven at 40 °C to dryness. Prior to the catalytic tests the samples were dried at 120 °C in order to remove water of crystallization.

2.2. Characterization of catalysts

The specific surface areas of samples were calculated from the nitrogen adsorption–desorption isotherms at 77 K in an Autosorb-1, Quantachrome equipment. Prior to the measurements, the samples were preheated and degassed, under vacuum at 60 °C for 18 h. Morphology of polyaniline–sulfate was studied by means of Field Emission Scanning Electron Microscope JEOL JSM-7500 F.

The total amount of Brönsted acid sites was determined by acid-base titration following procedure previously described [18,27]. An amount of ca. 0.1 g of each sample was suspended in 20 cm^3 of NaOH (0.1 M) for 24 h at room temperature. The liquid sample obtained after polymer filtration was subsequently titrated with 0.1 M HCl.

Acid sites strength was determined with Hammett indicators by means of procedure used by other authors [43,44]. Approximately 25 mg of sample was shaken with 1 cm^3 of a solution of Hammett indicators diluted in methanol and left to equilibrate for 2 h after which no further color changes were observed. The color of the sample was then noted. The following Hammett indicators were used: 4-(dimethylamino)azobenzene ($pK_a = +3.3$), 4-phenylazodiphenylamine ($pK_a = +1.5$), crystal violet ($pK_a = +0.8$), dicinnamalacetone ($pK_a = -3$), anthraquinone ($pK_a = -8.2$), 4-nitrotoluene ($pK_a = -11.35$), 3-nitrotoluene ($pK_a = -11.99$), 1-chloro-4-nitrobenzene ($pK_a = -12.70$), 1-chloro-3-nitrobenzene ($pK_a = -13.16$), 1.4-dinitrotoluene ($pK_a = -13.75$). The acid strength is quoted as being stronger than the weakest indicator which exhibits a color change, but weaker than the strongest indicator that gives no change.

The contact angles (α) were measured with use of an optical goniometer (Cobrabid Optica, Poland) with a digital camera installed in axial extension of its lens. The liquid droplets of the constant volume (3–5 μl) were introduced onto the surface of studied samples with micropipette. The catalyst was in the form of pressed tablet, ca. 0.5 cm in diameter and 0.1–0.2 cm thick. The measurement was taken at 21 °C. The values of contact angles were found from the geometric analysis of pictures taken for liquid droplets, which involved the use of original software developed by Kontrast (Pasłęk, Poland) for the interpretation of Young's equation. Nine (9) droplets were analysed each time which were placed on the surface simultaneously. For each picture recorded, the geometrical shape analysis was repeated ten times.

2.3. Catalytic tests

The transesterification of triglycerides, triacetin (Fluka) and castor oil (Microfarm, Poland) with methanol was carried out in a 100 cm^3 glass reactor at atmospheric pressure following the procedure reported in our previous papers [32,34]. Reactor was equipped with a reflux condenser, magnetic stirrer, and a tube for sampling the solution. In catalytic experiment, triacetin or castor oil, methanol and internal standard (toluene or eicosane) were introduced to the reactor, heated up to a given temperature and then the catalyst was added.

For transesterification of triacetin 2.6 cm^3 of triacetin and an excess of methanol 16.2 cm^3 were used. This composition corresponds to typical molar ratio of methanol to triacetin (MR) equal to 29 which was commonly used in our previous studies. The mixture was heated to the desired temperature (50 °C), and then 0.3 g of catalyst was added, (if not otherwise mentioned) and stirred continuously. This amount of catalyst corresponds to catalysts concentration in the reaction mixture equal to 15.8 $\mathrm{g/dm}^3$.

In the course of catalytic tests the samples of reaction mixture were periodically taken and analysed by GC method following the method described earlier [32]. From the data of GC analysis the triacetin conversion (C_{TG}), and the yields of partial glycerides, diacetin, monoacetin (Y_i) were calculated as follows:

$$C_{\mathrm{TG}} = \frac{N_{\mathrm{TG},0} - N_{\mathrm{TG}}}{N_{\mathrm{TG},0}} \times 100\% \qquad (1)$$

$$Y_i = \frac{N_i}{N_{\mathrm{TG},0}} \times 100\% \qquad (2)$$

where $N_{\mathrm{TG},0}$ and N_{TG} are the moles of triacetin initially present in the reactor and the moles of triacetin remaining at time t, respectively; N_{DI} and $\mathrm{N}_{\mathrm{MONO}}$ are the numbers of moles of diacetin and monoacetin in the reactor at time t. The number of glycerol moles formed (N_{GL}) was calculated from the mass balance:

$$N_{\mathrm{GL}} = N_{\mathrm{TG},0} - (N_{\mathrm{TG}} + N_{\mathrm{DI}} + N_{\mathrm{MONO}}) \qquad (3)$$

The selectivity to diacetin (S_{DACT}), monoacetin (S_{MONO}) and to glycerol (S_{GL}) was calculated from the formula:

$$S_i = \frac{N_i}{N_{\mathrm{TG},0} - N_{\mathrm{TG}}} \times 100\% \qquad (4)$$

As a measure of catalyst activity initial rate of triacetin conversion (calculated at conversion below 10%) related to 1 g of catalyst was assumed [r, mol TACT/min g].

The transesterification of castor oil with methanol was performed at 60 °C using 6 g of castor oil, 7.6 cm^3 of methanol (MR = 29) and 0.6 g of catalyst. This amount of catalyst corresponds to catalysts concentration in the reaction mixture equal to 43 $\mathrm{g/dm}^3$.

Transesterification of castor oil at the same conditions as in case of triacetin (50 °C, low concentration of catalyst, 15.8 $\mathrm{g/dm}^3$) resulted in very low yield of methyl esters, practically not measurable for less active Cs-2.5 salt. This is a consequence of definitively lower rate of reaction involving bulky triglycerides of castor oil. Therefore, in order to have similar yields of methyl esters, ca. 40–60% after 3 h of methanolysis of both triglycerides, the transesterification of castor oil was carried out at temperature of 60 °C using higher concentration of catalysts, 43 $\mathrm{g/dm}^3$. This concentration was chosen in experiments with the most active Ag-2 catalyst.

The progress of castor oil methanolysis was monitored by GC analysis of methyl esters formed [32,34]. Castor oil was entirely composed of a triglyceride of ricinoleic acid (87.44 wt. %), traces of glycerol (below 0.1 wt %), di- and mono-glycerides of ricinoleic acid, and free ricinoleic acid (below 0.1 wt. %). From the GC analysis of methyl esters apart from the dominating triglycerides of ricinoleic acid, low amounts of triglycerides of other fatty acids (linoleic 5.05 wt.%, oleic 3.88 wt.%, stearic 1.4 wt.%, palmitic 1.28 wt.%, linolenic 0.56 wt.%, and other acids 0.39 wt.%) were determined in castor oil. and the average molecular weight of castor oil was calculated to be 928 g/mol [34]. In discussion of catalytic results, the yield of methyl esters formed in methanolysis of castor oil was taken into consideration, identically to method widely used in the case of vegetable oils. The yield of methyl esters formed in methanolysis of castor oil was expressed in terms of the percentage of methyl esters produced.

As a measure of catalyst activity initial rate of methyl esters (ME) formation (below 10%) related to 1 g of catalyst was assumed [r (ME), mol ME/min g].

The catalytic tests were performed 2 times (in selected cases 3 times) and the average values are reported. The precision of chromatographic analysis was 5%.

Table 1
Physicochemical characterization of catalysts properties.

Catalyst	Surface area [m^2/g]	Porosity [cm^3/g]	Acid capacity [mmol H^+/g]	Acid sites strength	(α-TACT)	(α-CAS)	(α-GL)
PANI-S	25.9	0.054	4.75	$1.5 < H_0 < 0.8$	12.1 ± 0.7	49.4 ± 1.6	53.5 ± 2.1
Amberlyst-15	41.6	0.24	4.70	$0.8 < H_0 < -3.0$	16.7 ± 2.3	36.3 ± 1.7	61.6 ± 3.4
Nafion SAC-13	164	0.56	0.15	$-12 < H_0 < -12.7$	22.1 ± 1.4	48.9 ± 2.3	61 ± 3.5
Cs-2	1		0.32	$-13.2 < H_0 < -13.8$	3.3 ± 0.1	42.3 ± 1.5	37.7 ± 2.1
Cs-2.5	136		0.16	$-13.2 < H_0 < -13.8$	7.3 ± 0.9	41.9 ± 2.5	39.8 ± 1.4
Ag-2	4.7		0.32	$-3.0 < H_0 < -8.2$	9.1 ± 0.2	43.1 ± 1.3	24 ± 1.7

3. Results and discussion

Physicochemical properties of studied catalysts are collected in Table 1. Among polymeric catalysts, Nafion-SAC-13 composite exhibits the highest specific surface area (164 m^2/g) and the highest porosity because the polymer is dispersed throughout the matrix of silica. Surface area and porosity of other two polymers, Amberlyst-15 and PANI-S are definitively lower and porosity is especially low in the case of PANI-S sample. In all polymeric catalysts a bimodal distribution of the pores is observed and mesopores with average pore diameters in the range of 9–18 nm dominate (Fig. 1). The SEM image of PANI-S powder is displayed in Fig. 2. An aggregated granular morphology typical of polyanilines is observed. In catalytic experiments the sieve fraction of particles of size 40–80 μm of Amberlyst-15 and Nafion-SAC-13 polymers was used.

Cesium and silver salts of HPW, although exhibit crystalline morphology in powdered state, they formed colloidal dispersion under conditions of triglyceride transesterification. Colloidal particles existing in reaction mixture were determined to be 300–600 nm in size [34]. As shown in Table 1, the catalysts essentially differ with respect to acid capacities. The concentrations of acid sites are high and comparable for Amberlyst-15 and PANI-S (4.70 and 4.75 mmol/g, respectively) and both capacities are distinctly higher than that of Nafion-SAC-13 composite (0.15 mmol/g). The concentration of acid sites in the HPW salts, were assumed to be the stoichiometric ones, according to the reports of other authors [30]. The catalysts differ also with respect to the strength of acid centres determined by Hammett indicators method. Among all studied catalysts, PANI-S is the catalyst with the weakest acid sites, the centres are stronger in Amberlyst-15 resin and much stronger are the sites in Nafion-SAC-13 composite. In all three HPW salts the acid centres are of higher strength than in polymeric catalysts. However, acid centres of Ag-2 salt exhibit weaker acidity compared to that of Cs salts which are known to be superacids [28,43]. The relation of acid sites strength determined for Ag and Cs salts agrees with the report of Moffat and coworker [45]. The physicochemical properties, among them capacity of acid centres and their strength determined in the present work for both commercial resins, Amberlyst-15 and Nafion-SAC-13 agree well with the data reported by other authors [18,46]. Acid capacity of 0.13–0.16 mmol/g was reported for Nafion-SAC-13 composite and 4.7 mmol/g for Amberlyst-15 resin [18,46].

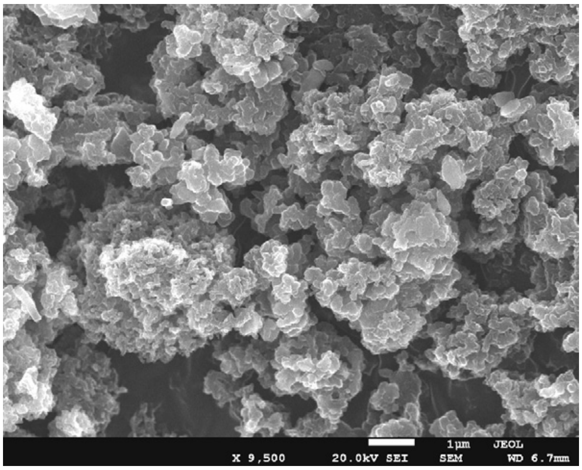

Fig. 2. SEM image of PANI-S.

In order to compare hydrophobic/hydrophilic nature of catalysts, studies were undertaken to evaluate their affinity to highly hydrophobic triglyceride reactant relative to that toward rather hydrophilic, glycerol. These studies included the transesterification experiments as well as physicochemical measurements.

Three series of catalytic experiments were performed. In all series, reaction was carried out under the same conditions. The catalytic tests of series I are methanolysis experiments performed with typical procedure described in Experimental. In series II experiments, known amounts of glycerol (corresponding to 50% and 100% of glycerol content formed in the experiment) were added to the reaction mixture prior to the catalytic experiment. After heating glycerol-containing reaction mixture up to the desired temperature (50 °C) the catalyst was introduced and the reaction was started. From these experiments, the affinity of catalysts toward interaction with glycerol can be compared. In order to compare the affinity of catalysts to triglyceride, series III experiments were performed, in which the sample of catalyst was contacted with triacetin (30 min, at 50 °C) before methanolysis reaction. These experiments were carried out in view of results reported by Liu et al. [47]. When hydrotalcite catalysts were pretreated by triglycerides prior to transesterification test, their activity dropped. According to the authors, this negative role of pre-adsorbed triglycerides resulting in drop of catalysts activity was associated with the strong adsorption of triglycerides on active sites [47].

The affinity of catalyst to non-polar triglyceride relative to that toward polar glycerol was also evaluated from the measurements of contact angles for droplets of triacetin (α-TACT), castor oil (α-CAS) and glycerol (α-GL) on the surface of pressed tablet of catalysts (Table 1). It should be noticed that in limiting case, if the liquid is very strongly attracted to the solid surface, the droplet will completely spread out on the solid surface and the contact angle will be close to 0°.

The measured values of castor oil contact angles (α-CAS) are of similar order for all studied catalysts, 36–49° and all are relatively low showing that droplets of castor oil are attracted to the surface of all catalysts (Table 1). This shows hydrophobic character of all studied catalysts. All studied catalysts exhibit also low triacetin contact angles (α-TACT) within the range 3–22° showing that the droplets of triacetin are well attracted to their surface. However, the values of triacetin contact angles (α-TACT) differ showing that the affinity of catalysts toward triacetin molecules varies. The strongest attraction of triacetin is observed for Cs salts (α-TACT = 3.3°) the catalysts with the strongest acid sites. It should be stressed that hydrophobic character of Cs-2.5 salt observed in the present work is consistent with the data of Okuhara and coworker [48] who termed this salt as “hydrophobic” solid catalyst from the measurements of its interactions with benzene. The attraction of triacetin is weaker in case of PANI-S and Amberlyst-15 polymers with weaker acid sites. The value of (α-TACT) for Nafion-SAC-13 is the highest, 22°,

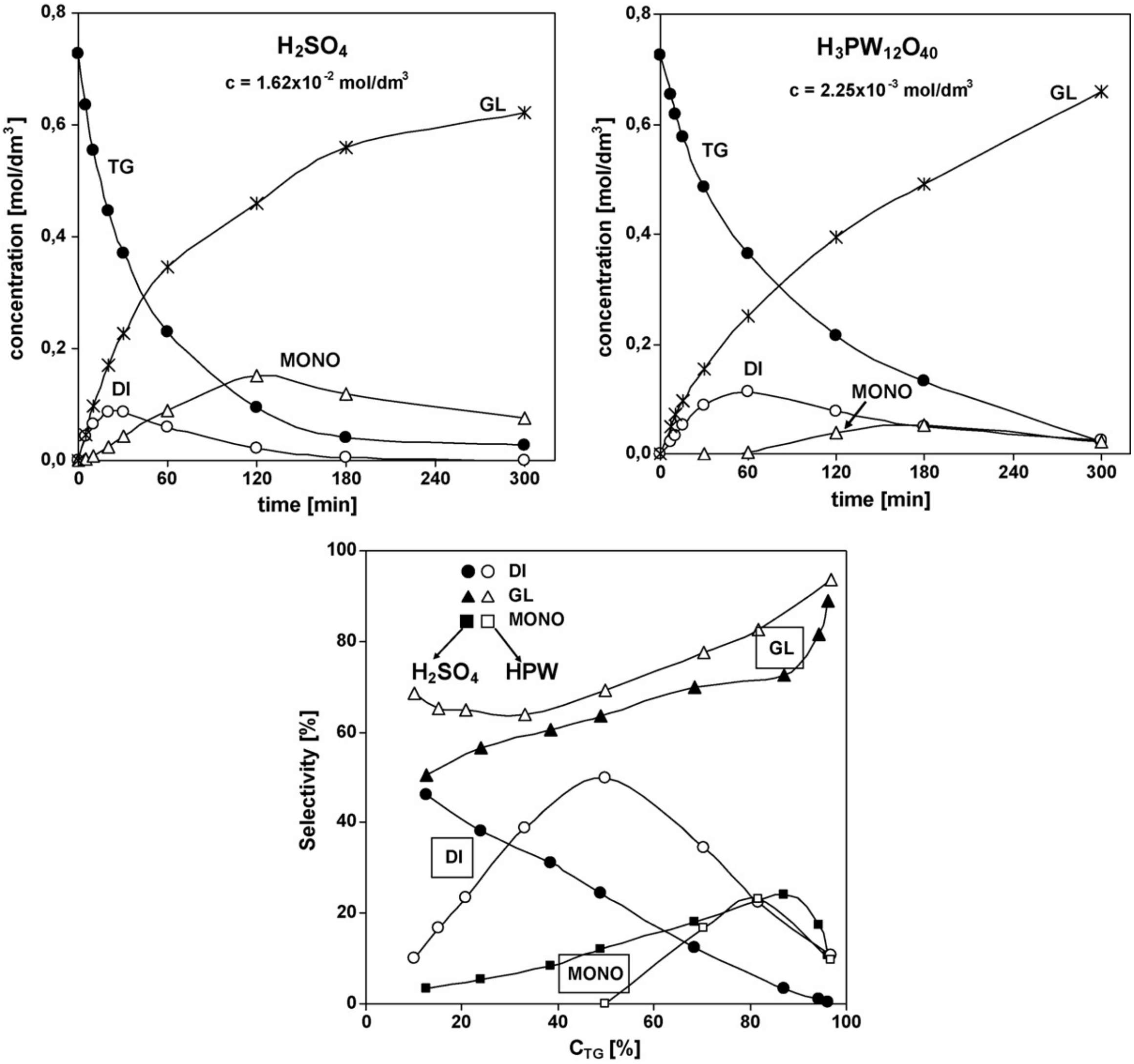

Fig. 3. Methanolysis of triacetin catalysed by soluble H_2SO_4 and $H_3PW_{12}O_{40}$ acids. Reagents distribution profiles and selectivity to glycerol (GL), diacetin (DI) and monoacetin (MONO) (reaction conditions: MR = 29, temp. 50 °C).

showing that triacetin is slightly weaker attracted to the surface of this composite maybe owing to the more polar Si–OH groups present in this composite. It seems from the obtained data that in the spreading of the droplets of triacetin, apart from "typical hydrophobic/hydrophilic interactions" also the acidity of catalyst surface played a role. On the other hand, the castor oil contact angles (α-CAS) are higher compared to the values of (α-TACT) and they do not allow determination of difference between properties of individual catalysts. This may be associated with high viscosity of castor oil (ca. 10 times higher compared to triacetin) and the presence of triglycerides consisting of C–OH groups.

As shown in Table 1, the catalysts strongly differ with respect to the glycerol contact angles (α-GL). For polymeric catalysts, the values of (α-GL) all are comparable and within the range 53.5–61.6° whereas all three salts of HPW, Ag-2, Cs-2 and Cs-2.5 have definitively lower glycerol contact angles, 24°, 37.7° and 39.8°, respectively. This shows that, glycerol is well attracted to the surface of all HPW salts, definitively better than to the surface of polymeric catalysts. Thus, all studied catalysts exhibit much better affinity to non-polar triacetin molecules than to the polar reagent, glycerol.

The activity of Amberlyst-15 and Nafion-SAC-13 catalysts was reported to be due to the acid centers, SO_3H [5] and that of PANI-S was associated with the presence of sulfuric acid [25,26] whereas in Cs and Ag salts of HPW, protons are the active centers [28,33]. Therefore, methanolysis experiments were performed in the presence of soluble H_2SO_4 and $H_3PW_{12}O_{40}$ acids (dried at 230 °C before experiment [32,49]). Product distribution profiles obtained are displayed in Fig. 3. They differ with respect to the course of consecutive reactions transforming triacetin via diacetin and monoacetin to glycerol. Similar difference was also observed upon transesterification of rapeseed oil catalysed by various soluble Keggin heteropolyacids and sulfuric acid, however, no comments were provided by the authors [49]. As Fig. 3 shows in the presence of sulfuric acid both partial glycerides, diacetin and monoacetin were formed from the very beginning of reaction and their contents passed through the maximum. The maximum content of diacetin is low 0.087 mol/dm^3 (corresponds to diacetin yield of 12%) and is reached at ca. 40% triacetin conversion whereas the maximum yield of monoacetin is very high. A different effect can be seen in the presence of soluble HPW. From the very beginning of reaction the only partial glyceride formed is diacetin which attained high maximum content, 0.112 mol/dm^3 (corresponds to diacetin yield of 15.5%) whereas, monoacetin is observed only at higher triacetin conversion, above 50% and its maximum content is very low (Fig. 3). This difference can be easier recognized from the graphs

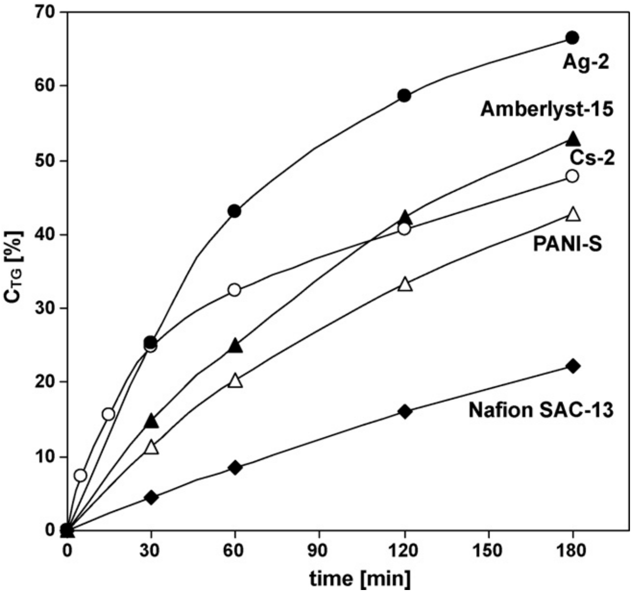

Fig. 4. Transesterification of triacetin in the presence of PANI-S, Amberlyst-15, Nafion-SAC-13, Cs-2 and Ag-2 catalysts (reaction conditions: MR = 29, temp. 50 °C, catalysts concentration 15.8 g/dm^3).

reporting the selectivity to glycerol and partial glycerides. From the very beginning of reaction up to 30–40% triacetin conversion, the selectivity to glycerol is as high as 65% over HPW whereas the selectivity is lower ca. 50% in sulfuric acid catalysed transesterification. An opposite relation is observed for selectivity toward diacetin. Thus, from the very beginning of transesterification catalysed by soluble HPW, the fraction of triacetin reacted to glycerol was higher than in the presence of sulfuric acid. This effect may be related to some of properties of studied acids and in particular higher strength of acid protons in $H_3PW_{12}O_{40}$ may be taken into account [28]. It has also been reported that due to higher acid strength of HPW at equivalent H$^+$ concentrations HPW-catalysed transesterification achieves higher reaction rates than conventional mineral acids (H_2SO_4, H_3PO_4) [32,49].

Owing to a difference in performance of H_2SO_4 and $H_3PW_{12}O_{40}$ acids, the results obtained on polymeric catalysts are compared with that for H_2SO_4 and catalytic performance of Ag and Cs salts is compared with that of soluble $H_3PW_{12}O_{40}$.

3.1. Series I experiments

Fig. 4 shows the time conversion plots for transesterification of triacetin. All catalysts are effective for the methanolysis of triacetin. As a measure of catalyst activity, initial rate of triacetin conversion (below 10% conversion) per unit mass of catalyst was assumed (Table 2). Taking into consideration initial rate per unit

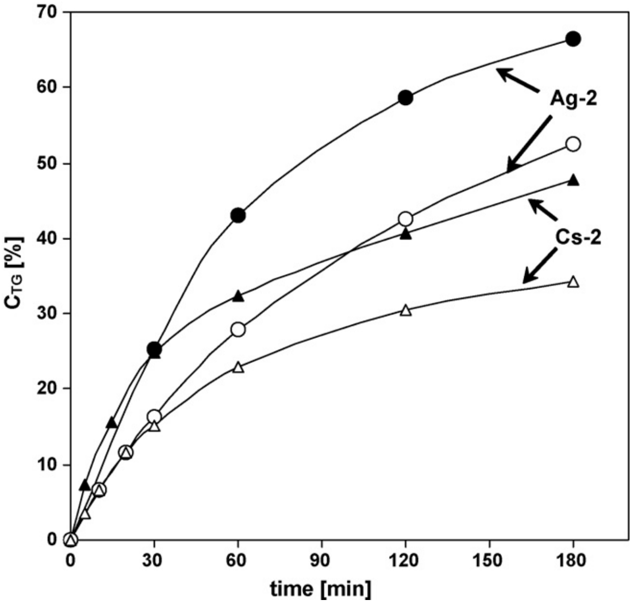

Fig. 5. Transesterification of triacetin in the presence of Cs-2 and Ag-2 salts at catalyst concentration of 7 g/dm^3 (open marks) and 15.8 g/dm^3 (full marks) (reaction conditions: MR = 29, temp. 50 °C).

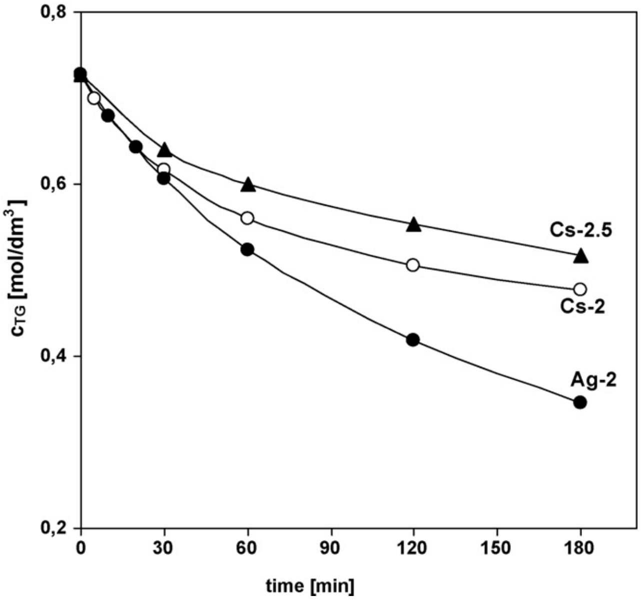

Fig. 6. The change of triacetin concentration in methanolysis catalysed by Cs-2, Cs-2.5 and Ag-2 salts (reaction conditions: MR = 29, temp. 50 °C, catalysts concentration 7 g/dm^3).

Table 2
Initial activity of catalysts in transesterification of triacetin and castor oil and the drop of initial rate induced by glycerol and triacetin.

Catalyst	Maximum conversion [%]	Maximum yield [%]	R [mol(TACT) min^{-1} g^{-1}] 10^{-4}	Activity drop [%]			r [mol(ME) min^{-1} g^{-1}] 10^{-4}
				Triacetin pre-treatment	Glycerol (50%)	Glycerol (100%)	
PANI-S	99	96.4	1.76	21	8	13	0.120
Amberlyst-15	98.8	96.5	2.26	19	9	22	0.125
Nafion-SAC-13	86.2[a]	70.4[a]	0.61	35	39	70	0.035
Cs-2	94.6	91.1	7.28	45	69	83	0.420
Cs-2.5			4.0	46	75	87	0.088
Ag-2	92.6	94.1	5.10			58	0.760

[a] Determined after 30 h of reaction.

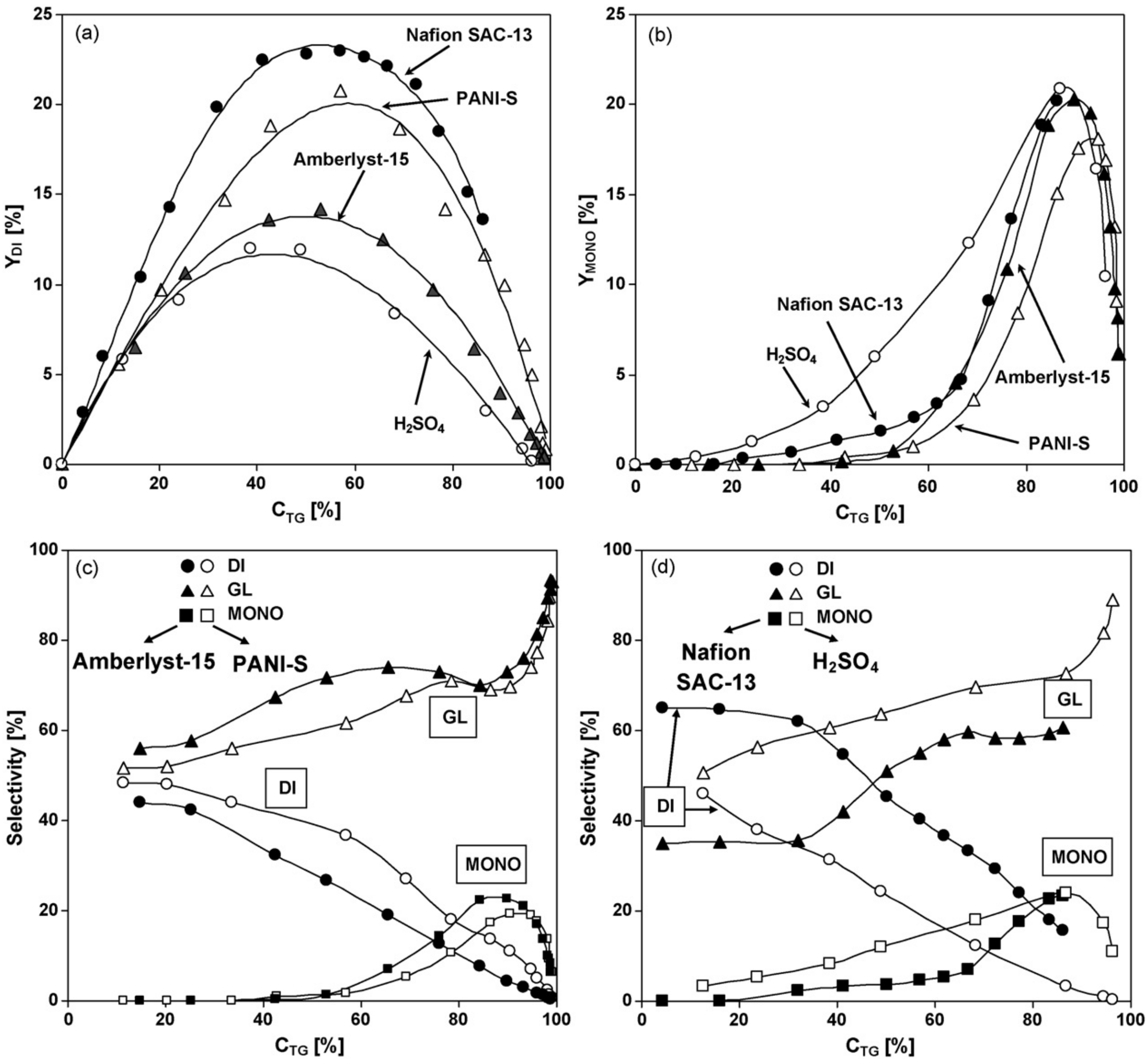

Fig. 7. Transesterification of triacetin catalysed by PANI-S, Amberlyst-15, Nafion-SAC-13 and soluble H_2SO_4. The yield of diacetin (a) and monoactin (b) vs. conversion of triacetin, selectivity to glycerol (GL), diacetin (DI) and monoacetin (MONO); (c and d) (reaction conditions: MR = 29, temp. 50 °C, solid catalyst concentration 15.8 g/dm^3).

mass of catalysts, Cs and Ag salts of HPW exhibited superior initial activity compared to all polymeric catalysts and the most active are Cs salts. Among polymeric catalysts the most active is Amberlyst-15 resin. The initial rate of triacetin conversion in the presence of Amberlyst-15 (2.26 mol min^{-1} g^{-1}) is only slightly higher than the rate on PANI-S (1.76 mol min^{-1} g^{-1}) but both rates are distinctly higher than the rate in the presence of Nafion-SAC-13 composite.

It should be remembered that catalyst activity is a function of both acid site strength and concentration. Amberlyst-15 and PANI-S catalysts, exhibit high and comparable concentrations of acid centres, but these sites are weak. On the other hand, the concentration of acid centres in Nafion-SAC-13 is distinctly lower (0.15 mmol/g) but these centres are of higher strength. This may explain the observed order of activity.

It can be observed that although the concentrations of acid sites in Nafion-SAC-13 and Cs-2.5 are similar (0.15 and 0.16 mmol/g, respectively) performance of Cs-2.5 differs significantly from that of Nafion-SAC-13. This may be related to the strength of sites, which are stronger in Cs-2.5 salt. Furthermore, it can be observed from the time conversion plots (Fig. 4) that catalytic performance of Cs-2 salt remarkably differs from that of Ag-2 salt and all other studied catalysts. Initially high activity of Cs-2 salt slowly decreases when ca. 20–30% of TACT was reacted and reaction progresses further at distinctly lower rate. This difference can be better recognized from graphs displayed in Fig. 5. The time conversion plots obtained at two different concentrations of Cs-2 salt in reaction mixture are compared with the results obtained at the same concentrations of Ag-2 salt. A difference in performance of Ag-2 and Cs-2 salts can be seen at both concentrations of catalysts. Analogous effect, decrease of initially high activity is also observed for Cs-2.5 salt. The decrease of triacetin concentration vs. time of reaction carried out in the presence of Cs-2, Cs-2.5 and Ag-2 salts is compared in Fig. 6. An inhibition of triacetin conversion is observed on both Cs-2 and Cs-2.5 salts, which makes their performance different from that of Ag-2 salt.

It should be noticed that although initially high rate on Cs salts decreases and further reaction progresses at lower rate, high conversion of triacetin (94.6%) was obtained on these salts. However, at the same reaction conditions this conversion on Cs-2 salt was reached after 15 h of reaction, i.e. 5 times longer reaction time compared to Ag-2 salt (3 h). This may suggest a partial blockage of active sites in the Cs salts during the transesterification of triacetin. This deactivation behaviour is observed for Cs salts only.

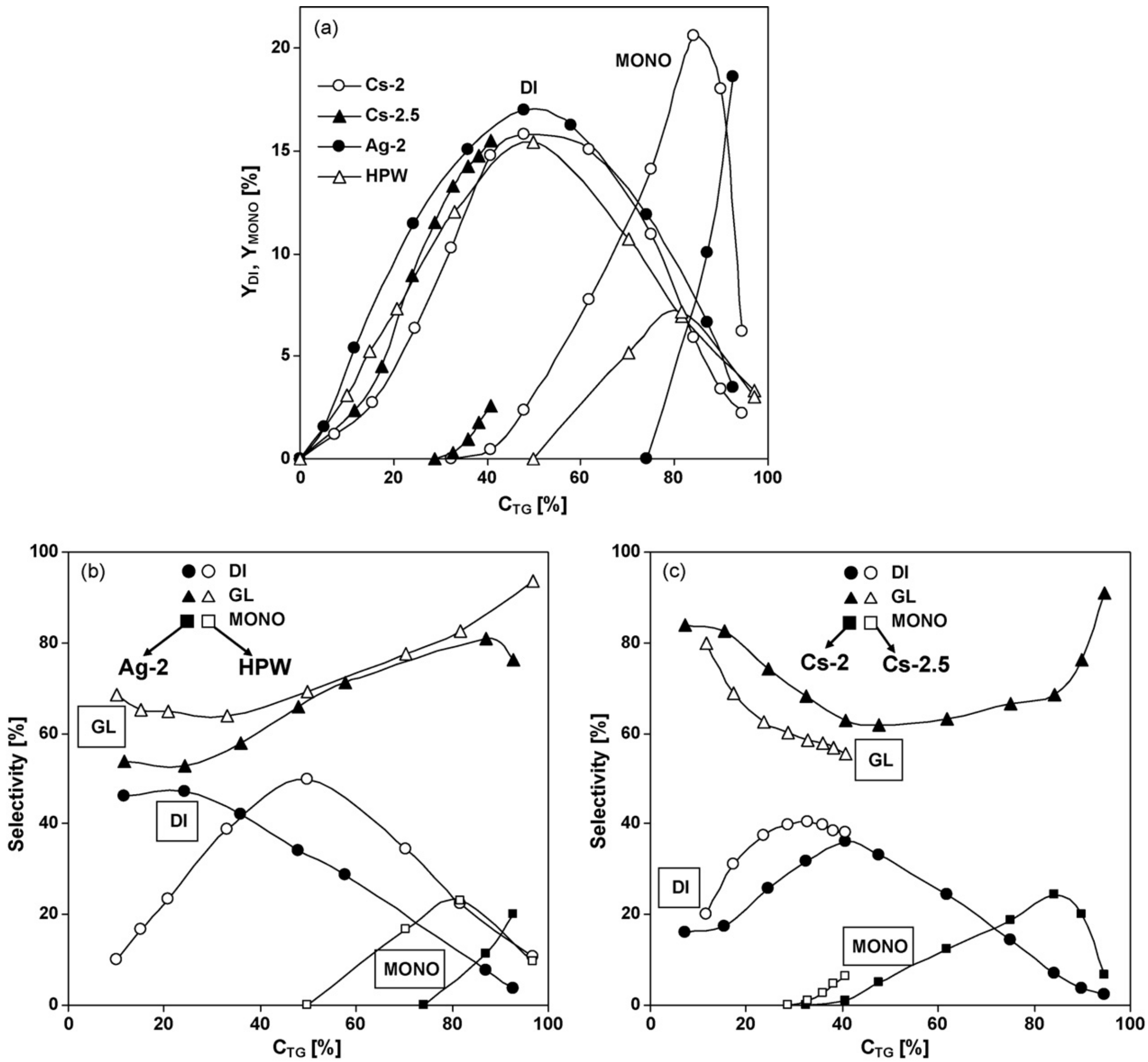

Fig. 8. Transesterification of triacetin catalysed by Cs-2, Cs-2.5, Ag-2 and soluble $H_3PW_{12}O_{40}$. The yield of diacetin and monoactin (a) vs. conversion of triacetin, selectivity to glycerol (GL), diacetin (DI) and monoacetin (MONO) (b and c) (reaction conditions: MR = 29, temp. 50 °C, concentration of HPW salts 15.8 g/dm^3).

In Fig. 7 the yields of partial glycerides (diacetin, monoacetin) are plotted vs. the conversion of triacetin for reactions performed in the presence of polymeric catalysts and soluble H_2SO_4. In the presence of all three polymeric catalysts the yield of diacetin is higher and that of monoacetin is lower compared to those under homogenous conditions using sulfuric acid. The selectivity data towards glycerol and partial glycerides are compared in Fig. 7c. Selectivity changes over Amberlyst-15 and PANI-S catalysts are of similar character to that for soluble sulfuric acid. In all three reaction systems at triacetin conversion below 30–40%, selectivity to glycerol achieves 50–60% and slowly increases as the reaction progresses. The course of consecutive reactions on Nafion-SAC-13 composite differs to some extent because selectivity to glycerol is lower (ca. 35%) and that to diacetin is higher. This shows that the course of consecutive reactions leading to glycerol is more restricted on Nafion-SAC-13 than on other two polymers maybe because of higher strength of acid sites and/or the presence of silanol groups in the composites. These results show that the transformation of triacetin via intermediates, diacetin and monoacetin to glycerol on solid catalysts changes relative to soluble H_2SO_4. In particular the higher yields of diacetin are observed in the presence of all three polymeric catalysts. This may be explained by an influence of hydrophobic environment of active centers in polymeric catalysts which in agreement with Liu et al. [36] can make more difficult further transformation of more polar molecules of partial glycerides, diacetin and monoacetin to glycerol.

In Fig. 8 the yields of partial glycerides obtained using Ag and Cs salts are compared with those in the presence of soluble $H_3PW_{12}O_{40}$. In all reaction systems diacetin is formed from the very beginning of reaction. The maximum yield of diacetin on Ag-2 salt is higher compared to soluble HPW whereas on Cs-2 salt the maximum yields are comparable. However, the growth of diacetin yield relative to soluble HPW is smaller than in case of polymeric PANI-S and Nafion-SAC-13 catalysts. In the presence of Cs salts the content of diacetin grows along to “S-shape curve”, which differs their performance from that of HPW and Ag-2 salt. A difference can also be observed in the yield of monoacetin. In the presence of Cs salts, monoacetin is formed at low triacetin conversion ca. 30%, which is definitively lower compared to soluble HPW (ca. 50%). In contrast, on Ag-2 salt monoacetin is formed at very high triacetin conversion. This difference in performance of Ag-2 and Cs salts resulted in quite different changes in selectivity to glycerol.

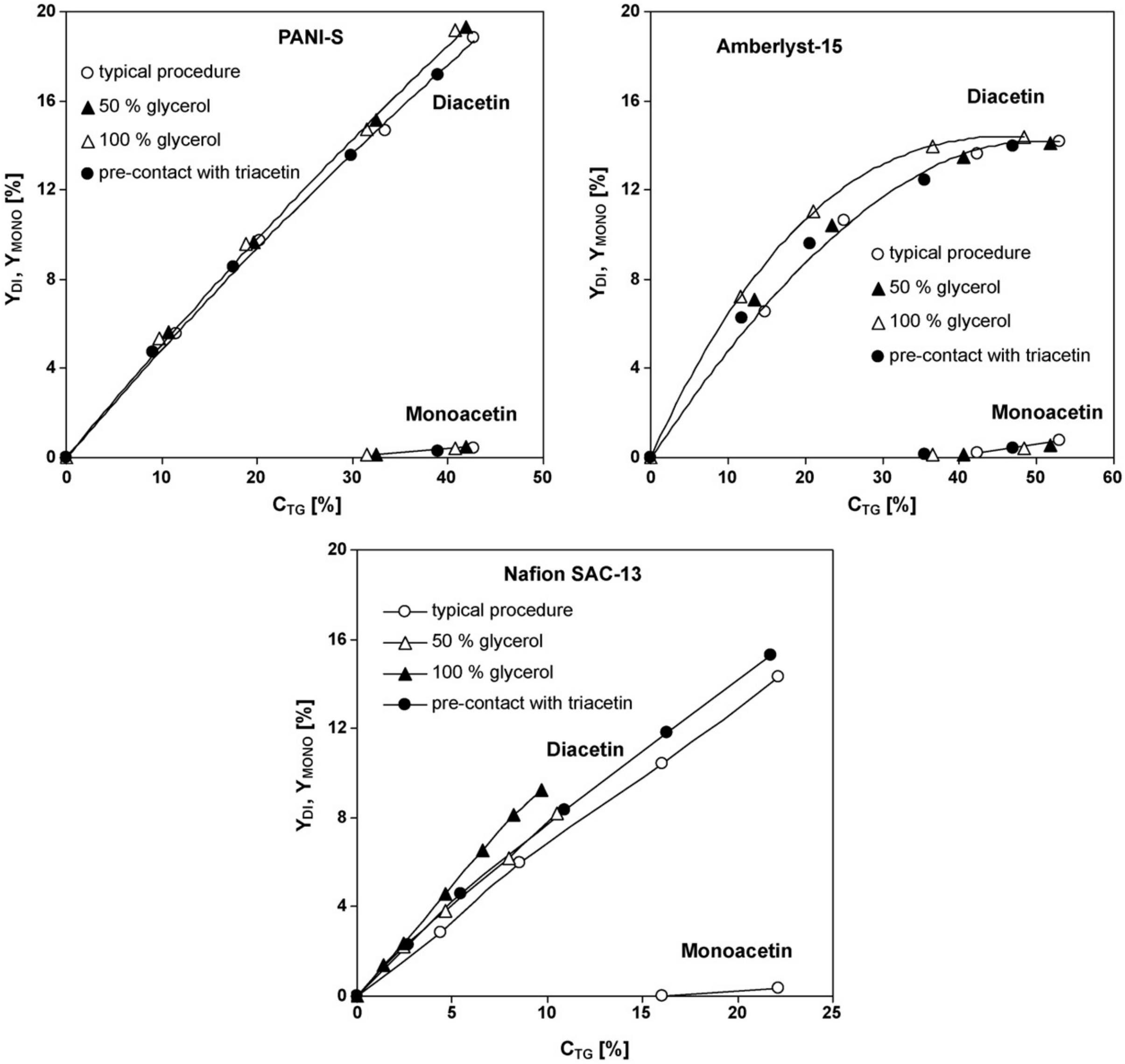

Fig. 9. The effect of glycerol and triacetin-pretreatment on the yield of diacetin and monoacetin, reactions catalysed by PANI-S, Amberlyst-15, Nafion-SAC-13 (reaction conditions: MR = 29, temp. 50 °C, catalyst concentration 15.8 g/dm^3).

As shown in Fig. 8b, from the very beginning of reaction on Ag-2 salt selectivity to glycerol is ca. 50% and it changes in similar manner to that on PANI-S and Amberlyst-15 polymers. On the other hand on Cs salts, selectivity to glycerol is very high, ca. 80%, higher than in the presence of soluble HPW. However, when ca. 20–25% of triacetin was reacted, selectivity to glycerol slowly decreases maybe due to the growing content of monoacetin. These effects may suggest strong interaction of partial glycerides/glycerol with active centers of Cs salts. This interaction may facilitate the transformation of diacetin to monoacetin as well it may facilitate the reverse reaction, transformation of diacetin to monoacetin (Fig. 8a). On the other hand, very high initial activity of Cs-2 salt remarkably decreased when ca. 20–25% of triacetin was reacted (Fig. 4). Thus, strong interaction between active centers (protons) of Cs salts and molecules of glycerol/partial glycerides may be considered as the reason of partial deactivation of Cs salts which started already at low conversion of triacetin, ca. 20–25%. This type behavior was not observed for Ag-2 salt and all other studied catalysts. Comparison of reagents distribution profiles on Ag-2 and polymeric catalysts (Fig. 7) with those on Cs salts (Fig. 8) show a difference in the course of consecutive reactions. In the former case, the yield of diacetin is higher and selectivity to glycerol is lower compared to Cs salts. This shows that on Cs salts the conversion of triacetin via di- and mono-glycerides to final product, glycerol is easier and the course of consecutive reactions is less inhibited. As already described, this inhibition leading to growing content of diacetin was to some extent influenced by hydrophobic properties of catalyst. Hence, the presence of acid sites of high strength, as in the Cs salts, seems to be more decisive than hydrophobicity of the nearest environment of these acid sites.

Now, the question arises as to whether the interaction of catalyst with glycerol impacts their activity. To verify this effect, series II experiments were performed in which reaction was carried out in the presence of glycerol. As described before, known amounts of glycerol (corresponding to 50% and 100% of glycerol content which can be formed in the experiment) were added to the reaction mixture before the catalytic experiment. In Table 2, the drop of initial rate (in %) relative to the rate obtained under typical procedure of catalytic test (series I) is reported. It is observed that added glycerol exerts only slightly the activity of polymeric catalysts, Amberlyst-15 and PANI-S because their activity dropped by ca. 8–9% only. In the presence of added glycerol the course of

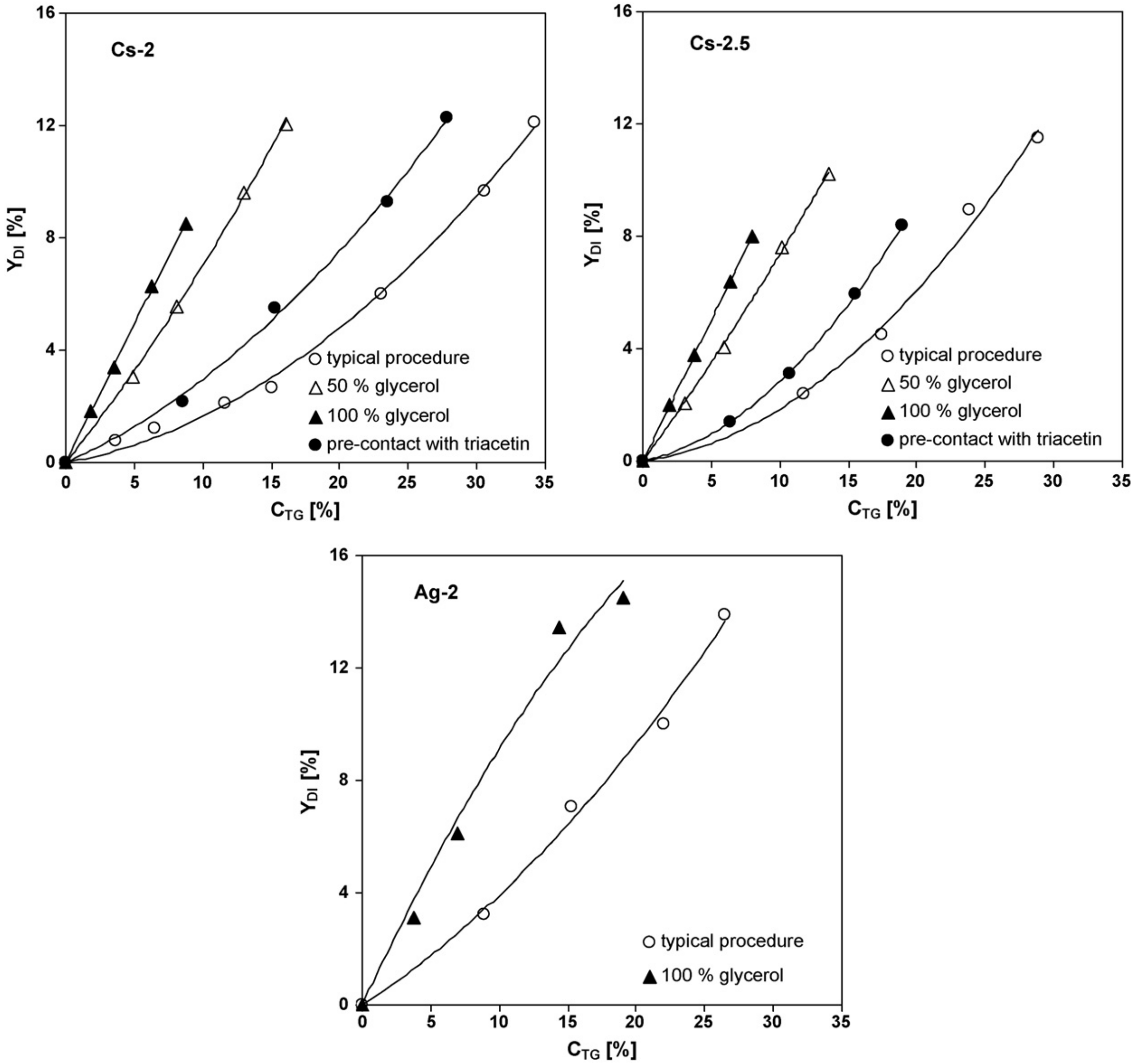

Fig. 10. The yield of diacetin in methanolysis catalysed by Cs-2, Cs-2.5 and Ag-2 salts. The role of glycerol and triacetin pre-treatment (reaction conditions: MR = 29, temp. 50 °C, catalyst concentration 15.8 g/dm^3).

consecutive reactions on PANI-S does not essentially change, evidenced by practically the same yield of diacetin. The changes are slightly higher on Amberlyst-15 resin (Fig. 9). The drop of activity was higher for Nafion-SAC-13 catalyst (by 39%) and the growth of diacetin yield was higher. Deactivation was the strongest for Cs-2 and Cs-2.5 salts, their activity dropped by 69% and 75%, respectively. In their presence, conversion of triacetin was suppressed from the very beginning of reaction [50]. Furthermore, as shown in Fig. 10, the yield of diacetin was much higher than in reaction without added glycerol.

The observed deactivation of catalysts due to added glycerol correlates with the strength of acid sites and the affinity of catalysts toward glycerol which was characterized by glycerol contact angles. The effect of glycerol is the smallest for PANI-S and Amberlyst-15 catalysts. Weak attraction of glycerol to the surface of such two polymers (α-GL equal to 61.6 and 61, respectively) is observed and both catalysts have weak acid centers. Although Nafion-SAC-13 have similar α-GL = 61°, its acid centers are stronger and deactivation due to added glycerol was higher.

The effect of added glycerol was the strongest for Cs salts. Glycerol was very well attracted to the surface of Cs salts and the active centers of these catalysts exhibited the highest strength. This resulted in the strongest deactivation of Cs salts. On the other hand, although glycerol was well attracted to the surface of Ag-2 salt, its acid centers are weaker and deactivation due to added glycerol was smaller. Thus, acid centers of high strength may be considered as factor facilitating interaction with polar reagents such as glycerol.

Similar effect, strong interaction with active centers and accumulation of partial glycerides/glycerol was observed on alkaline Mg-Al hydrotalcites [51] as well as on alkali supported on CaO and MgO catalysts [52]. The authors concluded that accumulation of polar reagents (glycerides/glycerol) could result in the creation of glycerol film onto the solid catalyst. The presence of this glycerol/glycerides film could have two important effects. It could present a mass transfer barrier to the methanol and triglycerides. Furthermore, it could facilitate the reverse reactions thus shifting reactions to left, to the intermediate products i.e. partial glycerides [52]. This type of effects seems to be very probable also in the presence of Cs salts.

Series III experiments were performed in the presence of catalysts pretreated with triacetin, i.e. non-polar reagent. The triacetin pretreatment was carried out at temperature of reaction, 50 °C.

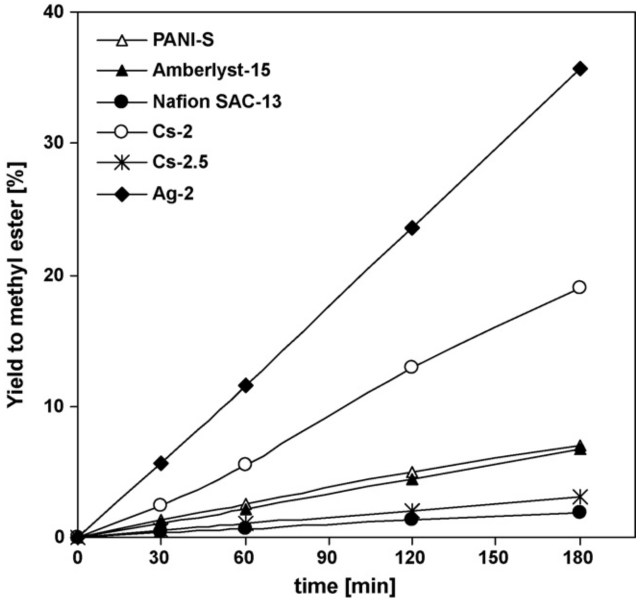

Fig. 11. The yield of methyl esters against reaction time, methanolysis of castor oil, reaction conditions: MR = 29, temp. 60 °C, catalyst concentration 43 g/dm^3).

The activity of all triacetin-pretreated catalysts dropped but to various extents (Table 2). Similar effect, the drop of activity was reported by Liu et al. [47]. It is observed that deactivation was low for PANI-S and Amberlyst-15 catalysts, 21% and 19%, respectively. Deactivation of Nafion-SAC-13 composite was stronger (ca. 35%) and deactivation was the strongest in case of Cs salts. Their activity dropped by ca. 45%. An influence of triacetin pretreatment on the yield of diacetin is reported in Figs. 9 and 10. The yield of diacetin practically does not change in the presence of triacetin-pretreated PANI-S and Amberlyst-15 catalysts, grows only slightly in the presence of Nafion-SAC-13 composite. The increase of diacetin yield is the highest on Cs-2 and Cs-2.5 salts however, this increase is lower compared to that induced by added glycerol (Fig. 10). Hence, the obtained order of activity drop correlates with the strength of acid sites determined by Hammett indicators for studied catalysts. An exception is Nafion-SAC-13 composites, maybe because of the presence of more polar silanol groups.

Let us compare the activity of studied catalysts in the transesterification of vegetable oil, castor oil. As a measure of catalyst activity initial rate of methyl ester formation (r (ME), mol min^{-1} g^{-1}) was assumed (Table 2). The yield of methyl esters against reaction time is shown in Fig. 11. For polymeric catalysts the order of activity is the same as that observed in methanolysis of triacetin. The activities of Amberlyst-15 and PANI-S are higher than that of Nafion-SAC-13. Moreover, activity of Nafion-SAC-13 is the lowest, ca. 3.7 times lower than that of Amberlyst-15 (3.6 times lower in methanolysis of triacetin). In contrast to polymeric catalysts, the activity relations changed for Cs, Ag salts of HPW (Fig. 11). In the presence of Ag-2 salt methanolysis of vegetable oil is faster reaction than on Cs-2 and Cs-2.5 salts. In addition, the activity of Cs-2 salt is ca. 4 times higher than that of Cs-2.5 whereas in methanolysis of triacetin Cs-2 was only 1.8 times more active than Cs-2.5 salt. This may be explained taking into account that the accessibility of large triglyceride molecules present in castor oil to the active sites is more difficult and the activity under these conditions may be mainly related to the centers in outermost surface of catalysts particles. Under these conditions the centers may be deactivated due to glycerol already from the very beginning of the transesterification. As a consequence, activity of Cs salts is low from the very beginning of castor oil transesterification.

In conclusions, all studied catalysts exhibit better affinity toward highly hydrophobic triglycerides reactants compared to that toward rather hydrophilic glycerol. The affinity of catalysts to glycerol differs being the highest for the Cs and Ag salts of HPW. Therefore affinity of studied catalysts toward glycerol and the strength of acid sites seem to be decisive factors for their activity and in particular for deactivation due to polar reagents adsorption. Greater affinity toward glycerol and higher strength of acid sites will result in easier deactivation of catalysts. However, the comparison of results for Ag-2 and Cs-2 salts shows that the strength of acid sites seems to be more important than the affinity toward glycerol. This conclusion is supported by the observation that glycerol was better attracted to the surface of Ag-2 salts compared to Cs-2, however, due to weaker acid sites deactivation of Ag-2 salt was negligible. The results obtained in this work well support literature suggestions/observations that a moderate strength of acid sites and their hydrophobic microenvironment should promote the activity and stability of solid acid catalysts in reaction mixture consisting of methanol and triglyceride [5,24].

4. Conclusions

Transesterification of triacetin with methanol was studied in the presence of solid acid catalysts Amberlyst-15, Nafion-SAC-13, polyaniline-sulfate, $Ag_2HPW_{12}O_{40}$, $Cs_2HPW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. The initial activity per unit mass of catalyst in reaction of triacetin was the highest for Cs salts, $Cs_2HPW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ however, the catalysts partially deactivated in the course of reaction. The highest strength of acid sites and high affinity toward polar glycerol was determined for these Cs salt. The affinity of catalyst to highly hydrophobic triglyceride reactant relative to that toward rather hydrophilic glycerol was found to affect the course of consecutive reactions transforming triacetin via partial glycerides (diacetin, monoacetin) to final product, glycerol. Furthermore, affinity of studied catalysts toward glycerol and the strength of acid sites seem to be decisive factors for their activity and in particular for deactivation due to polar reagents adsorption. Greater affinity toward glycerol and higher strength of acid sites, deactivation of catalysts would be easier. The results obtained in this work well support literature suggestions/observations that a moderate strength of acid sites and their hydrophobic microenvironment should promote the activity and stability of solid acid catalysts in transesterification of triglycerides.

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