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Catalytic aspects of biodiesel fuel byproduct valorisation

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ABSTRACT

A series of modified montmorillonites pillared with ZrO_2 or variously prepared TiO_2 and impregnated with CuO were synthesised, characterized (BET and pore analysis, XRD, TPD, TPR, AAS) and tested in the reaction of catalytic dehydration of glycerol. It was found that catalytic performance was sensitive to the preparation procedure. The acidity resulted in higher initial conversion and higher initial selectivity to acrolein, whereas CuO was found to stabilize higher conversion and to change the product distribution, favouring formation of hydroxyacetone. Titania-pillared, CuO-impregnated montmorillonite showed a long-term selectivity to hydroxyacetone higher than 60% at 74% conversion.

1. Introduction

Within the last decade an increased interest in processes of conversion of biomass and biomass-derived products into fuels and chemicals has been observed. Many chemical compounds are currently industrially produced from fossil resources. Their synthesis from biomass-based feedstocks would be not only economically viable, but would also allow reusing these biomass feedstocks, which are currently often treated as waste product. One of such processes is the conversion of crude glycerol, manufactured during the biodiesel production, into valuable chemicals. The rapid increase of biodiesel production in the last decade caused the large surplus of glycerol at global markets. Hence, the invention of new applications for crude glycerol remains crucial for balancing its overproduction. Some possible processes utilizing glycerol include esterification, etherification, steam reforming [1–3] or catalytic dehydration to acrolein and hydroxyacetone. The latter reaction was investigated in this study. Numerous types of acidic catalysts were considered for the reaction of glycerol dehydration, such as zeolites, heteropolyacids and various acidic oxides [4–6]. However, they were often found to have disadvantages such as rapid deactivation, low hydrothermal stability, leaching of the active material and high price. In this work new types of catalysts, based on pillared clays, were synthesized and tested in the above-mentioned reaction. Montmorillonites were chosen for this study, as they can be easily modified to obtain texture, acidity and redox properties appropriate for dehydration of glycerol.

2. Experimental

2.1. Catalysts preparation

Pillared clays were prepared for this study by intercalation of commercial clay (Montmorillonite K5, Fluka, designated M) with zirconia-oligomeric solution, or one of two differently prepared titania-oligomeric solutions. Zirconia-oligocations were prepared from $ZrOCl_2{\cdot}8H_2O$ (Sigma–Aldrich, 98%). The pillaring agent (0.35 M Zr^{4+}) was then added to wet montmorillonite with the ratio of 55 cm^3/g clay, and stirred for 1 h at 70 °C. Pillaring by titania oligocations was carried out by method A or B. In method A, titania-oligocationic solution (0.82 M Ti^{4+}) was prepared from $TiCl_4$ (Fluka, >98%), then added to clay suspension (21 cm^3/g clay) under vigorous stirring for 4 h and subsequently aged for 12 h. In method B, titania-oligocationic solution was prepared from titanium tetraisopropoxide (Aldrich, 97%), according to the procedure described by Ooka et al. [7]. After intercalation all clays were washed with distilled water, centrifuged and dried at room temperature. In the next step, Cu^{2+} from $Cu(NO_3)_2$ was introduced onto pillared clays by the incipient wetness method. Flame atomic absorption spectrometry (F-AAS) verified copper content as $4.45\%_{wg}$ and $4.54\%_{wg}$ for M-TiO_2A–CuO and M-ZrO_2–CuO. Then samples were dried at room temperature and calcined at 480 °C in air.

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2.2. Characterization

The following physicochemical properties of the catalysts were determined: texture, structure, acidity and type/number of redox sites. BET surface area, total pore volume and average pore diameters of the samples were determined by low-temperature nitrogen sorption, using a Micrometrics ASAP 2000. Before measurements samples were outgassed at 300 °C for 1 h. The content of Cu in calcined catalysts was measured with F-AAS (Solaar 939, ATI Unicam). Long-range ordering was investigated by X-Ray Diffraction analysis (XRD7, Seifert GmbH) using Bragg–Brentano approach. Acidic properties of fresh and used catalysts were measured by temperature-programmed desorption of ammonia (TPD) as follows: at first samples were heated in a helium flow at 300 °C for 30 min, then cooled to 90 °C and 5 pulses of ammonia were added. Then the sample was flushed with a 50 cm^3/min helium for 45 min in order to remove physically sorbed NH_3. Subsequently, desorption was carried out with a heating rate of 10 °C/min up to 500 °C under flowing helium (50 cm^3/min). Ammonia signal (*m*/*e*: 16) was monitored with a MS detector (GSD 301, Pfeiffer Vacuum). Reducibility of the catalysts was examined by temperature programmed reduction (TPR) by heating in 8% H_2/Ar (flow, 50 cm^3/min; heating rate, 10 °C/min). The consumption of hydrogen was measured by thermal conductivity detector.

2.3. Catalytic test

Catalytic dehydration of glycerol was performed at atmospheric pressure in a fixed-bed flow reactor. The mixture of 200 mg catalyst and 200 mg inert quartz was heated to 280 °C and stabilized. The stream of the 5 wt.% glycerol (Merck) solution in water was metered with liquid flow controller (1 g/h) and evaporated at 180 °C in the controlled evaporator mixer (High-tech. CEM, Bronkhorst), entering the reactor in down-flow mode through thermostated capillary (190 °C) in a nitrogen flow (5 dm^3/h). The performance of the catalyst was determined at 280 °C. The water solution of reaction products was condensed in an ice-water trap and analyzed every hour with gas chromatograph (Chrompack 9001) equipped with a capillary column (30 m, ID: 0.32 mm, MACHERY-NAGEL) and a flame ionization detector (FID), using the following programme: 2 min isotherm at 120 °C, followed by heating 12 °C/min up to 245 °C and 5 min isotherm.

Conversion rate was calculated from the concentration of glycerol:

$$X = \frac{100 - c_{Glycerol}}{\sum_i c_i} \quad [\%]$$

where $c_{Glycerol}$ and c_i are the percent concentrations of glycerol and all other (*i*) species registered in a given gas chromatogram. Selectivity to acrolein and 1-hydroxyacetone was also calculated as:

$$S_{Acrolein} = \frac{c_{Acrolein}}{\sum_i c_i - c_{Glycerol}} \cdot 100\%$$

$$S_{Hydroxyacetone} = \frac{c_{Hydroxyacetone}}{\sum_i c_i - c_{Glycerol}} \cdot 100\%$$

where $c_{Acrolein}$ and $c_{Hydroxyacetone}$ are the percent concentrations of acrolein and hydroxyacetone.

3. Results and discussion

3.1. Texture

All adsorption–desorption isotherms were of type IV according to IUPAC classification. The distinct hysteresis loop was ascribed to the presence of mesopores of the slit-like shape. Textural properties of studied montmorillonites are summarized in Table 1. From Table 1 it can be seen that pillaring of montmorillonite with zirconium oxide decreased specific surface area from 199 to 177 m^2/g and increased slightly the mesopore volume from 0.20 to 0.24 cm^3/g. It can be also observed, that the impregnation of M-ZrO_2 with CuO further decreased surface area, which may be explained by blocking of the smallest pores with the CuO deposits. The pillaring of M with titanium oxide resulted in the increase of S_{BET} from 189 to 246 and 203 m^2/g, respectively, for pillaring by methods A and B. The total pore volume was also increased, proving the introduction of pillars between aluminosilicate layers, in good agreement with the literature [8]. The effect of the impregnation with CuO on the catalyst texture cannot be simply explained here by blocking of the part of the pores for both samples, as they behaved differently. M-TiO_2A–CuO showed a decrease of S_{BET} and very small changes in pore volume and mean pore size by impregnation, whereas the inserting of CuO into M-TiO_2B did not affect the surface area, but decreased the mesopore volume from 0.25 to 0.20 cm^3/g and the mean mesopore size from 49 to 39 Å. We proposed that the introduced CuO aggregates were smaller for the former catalyst, while for the latter there was a partial blocking of the pores by copper oxide.

The XRD studies show that there is no long-range ordering in the *c*-direction for all calcined samples, possibly due to the formation of delaminated structure.

3.2. Acidity

All TPD profiles had a maximum in the range of 150–250 °C, which allows classifying them as weak acid sites, according to Tanabe et al. [9]. The only exception was M-TiO_2A, which showed a broad (at least double) superimposed peak, which ended at ca. 370 °C. Thus, it may be classified as possessing also a considerable amount of acid sites of medium strength. The amount of adsorbed ammonia, calculated from the TPD-profiles, is presented in Table 1. Pillaring of M with the ZrO_2 or TiO_2B decreased the specific acidity of these two samples from 127 μmol NH_3/g to 108 or 89 μmol NH_3/g, respectively. On the other hand, the M-TiO_2A pillared support showed a considerable increase in acidity to 300 μmol NH_3/g. There seems to be a correlation with texture: the sequence of the number of acidic sites (per g) is similar as the sequence of S_{BET}. Possibly for M-TiO_2B and M-ZrO_2 some part of the pillaring compound was deposited on the catalyst surface as a non-framework species, blocking the smaller pores and the catalyst surface and, consecutively, diminishing the acidity of the samples. However, it may not be the only possible explanation, as it is believed that ZrO_2 itself shows weak acidic properties [10]. The next step of catalyst preparation – impregnation with CuO – brought about significant changes in catalyst acidity. The desorption profiles of the impregnated catalysts were higher than those of the appropriate supports. In case of M-TiO_2B–CuO and M-ZrO_2–CuO, there was ca. a double increase in the number of acidic sites. On the other hand, the desorption profile for M-TiO_2A–CuO was ca. 10% higher than that of the support, but it was narrower, and did not contain moderate acidic sites mentioned above. Hence, the total acidity of this sample was smaller (249 μmol NH_3/g) than the acidity of the support (300 μmol NH_3/g). Possibly some acidic sites of the support were blocked in the reaction with Cu^{2+} ions.

All catalysts were also studied by TPD-NH_3 after dehydration reaction of glycerol. The analysis showed, that the reaction caused partial decrease of total acidity for all samples with the simultaneous formation of medium–strong acid sites (ammonia desorption maximum at the range of 400–500 °C). The latter effect was most pronounced for M-TiO_2A catalyst. Because of the promisingly high starting acidity of this calcined sample, cat-

Table 1
Textural properties, acidity and TPR-H_2 peak maxima.

Sample	Specific surface area BET (m^2/g)	Mesopore volume (cm^3/g)	Mean mesopore diameter (Å)	NH_3-TPD acidity		TPR-H_2 peak maximum (°C)
				Total ($\mu mol\ NH_3/g$)	Intrinsic ($\mu mol\ NH_3/m^2$)	
M	190	0.20	42	127	0.67	–
M-ZrO_2	177	0.24	54	108	0.61	–
M-ZrO_2–CuO	157	0.23	59	215	1.37	232
M-TiO_2A	246	0.23	38	300	1.22	–
M-TiO_2A–CuO	218	0.22	41	249	1.14	189
M-TiO_2B	203	0.25	49	89	0.44	–
M-TiO_2B–CuO	204	0.20	39	212	1.04	210

alytic tests were conducted for longer time than in other cases. TPD of the sample after reaction was measured twice, showing that total acidity changed from 300 (calcined sample) to 101 and 156 $\mu mol\ NH_3/g$, respectively, after 24 and 72 h of the reaction run. When comparing intrinsic acidity ($\mu mol\ NH_3/m^2$), the catalysts form a sequence: M-ZrO_2–CuO > M-TiO_2A > M-TiO_2A–CuO > M-TiO_2B–CuO > M ≈ M-ZrO_2 > M-TiO_2B. The difference between acidity of a given support and the appropriate CuO-catalysts (i.e. M-ZrO_2 and M-ZrO_2–CuO; M-TiO_2A and M-TiO_2A–CuO; M-TiO_2B and M-TiO_2B–CuO) seems to suggest either a different distribution of CuO and/or the interaction between the support and active material.

3.3. Reducibility

Hydrogen consumption profiles of all Cu-containing samples presented clear, high and usually narrow peaks in region of 180–200 °C, which are responsible for reduction $Cu^{2+} \rightarrow Cu^0$. TPR peak maxima, shown in Table 1, occur between 180 and 240 °C. Additionally, at a higher temperature range (300–360 °C) the second, much broader peak was also present. The TPR measurements of unimpregnated supports were not conducted. It has been reported before [11], that the pillared montmorillonite showed negligible consumption of hydrogen in the mentioned temperature range.

Therefore it can be concluded, that all catalysts impregnated with CuO possessed at least two types of Cu oxides with different reducibility. According to Dow et al. [12], the first maximum can be ascribed to highly dispersed copper oxide, while the second – to bulky CuO. The intensity of the M-TiO_2A–CuO peak was ca. two times higher than for the other catalysts, suggesting that this sample contained the highest amount of the most easily reducible copper oxide species, while the second, broad peak was relatively small, indicating that the easily reducible copper oxide species dominated. The other two catalysts, M-ZrO_2–CuO and M-TiO_2B–CuO showed more pronounced presence of less reducible redox sites.

The TPR results suggest, that the quantity of the redox sites, as well as the reducibility of the Cu-containing catalysts depend strongly on the type of pillars and probably also on the support texture. Possibly M-TiO_2A support with the significantly higher specific surface area and also with higher acidity allowed the different dispersion of Cu species on the catalyst surface, and in consequence resulted in its easier reducibility.

3.4. Catalytic activity

Acrolein and hydroxyacetone were the predominant dehydration products detected in all the catalytic tests. Other identified by-products detected at low concentration included acetaldehyde, allyl alcohol, phenol, acrylic acid, CO_x, propionic acid, acetic acid, acetone and other. Fig. 1 presents results of the catalytic tests for the studied samples: calcined starting clay (M), pillared supports (M-ZrO_2, M-TiO_2A, and M-TiO_2B) and the CuO-impregnated catalysts in the form of dependence of both conversion and selectivity to acrolein and hydroxyacetone on the time-on-stream TOS.

The initially high conversion of the starting montmorillonite clay (M) dropped significantly after 3 h. This may be due to impurities (Fe_2O_3 and MgO) present, as reported elsewhere [13], in the initial clay at ca. 0.5–2%, which were removed during the synthesis of other catalysts. These additives were possibly removed from M during the dehydration reaction in presence of H_2O-stream or were irreversibly blocked by coke, and this would have a direct influence on rapid decrease of conversion. This catalyst showed, however, the highest selectivity to acrolein (over 50% after 7 h), and additionally a high selectivity to hydroxyacetone. The same trend of growing conversion to hydroxyacetone was also typical for catalysts impregnated with CuO: M-ZrO_2–CuO, M-TiO_2A–CuO, M-TiO_2B–CuO, as well as for the support of the latter sample, M-TiO_2B.

M montmorillonite pillared with different oligocations had diversified stability: initial conversion of M-TiO_2B was ca. 20% and remained unchanged after 7 h. M-ZrO_2 converted 75% of glycerol at the first hour of reaction, but after 7 h conversion had also decreased to ca. 20%. M-TiO_2A, however, sustained the 100% conversion of glycerol during first 7 h on stream. For this reason this catalyst was chosen for a long-term stability test, as discussed below.

All pillared montmorillonites had selectivity to acrolein ca. 20–30% after 7 h, which was lower than the starting clay. The production of hydroxyacetone, however, depended on the sample, with stable selectivity of 40% for M-ZrO_2 or 10% for M-TiO_2A and selectivity increasing from 30% to 60% after 7 h on stream for M-TiO_2B catalyst. The impregnation with CuO resulted in a significant improvement in conversion, with the exception of M-TiO_2A–CuO. The changes in acidity caused by introduction of CuO correlate well with the changes in conversion (cf. Fig. 1a). M-ZrO_2–CuO presented the best stability and conversion within the studied period (>90%). The initially complete conversion of glycerol over M-TiO_2B–CuO decreased to 60% during the reaction, whereas M-TiO_2A–CuO had the average conversion of ca. 70%.

Selectivity to acrolein was similar for all CuO-promoted montmorillonites, initially ca. 30%, and around 20% after 7 h TOS of dehydration reaction. The selectivity to hydroxyacetone was much higher, and, as already mentioned, increased with the reaction time, from 0%, 10% and 40% after first hour of the catalytic test, to 45%, 48% and 61% after 7 h, respectively, for M-ZrO_2–CuO, M-TiO_2B–CuO and M-TiO_2A–CuO. The observed effect of the increasing selectivity to hydroxyacetone may be explained by the formation of new acidic sites. As mentioned before, new medium to strong acidic sites were found for all studied catalysts after the reaction. This is in agreement with the work of Sato et al. [14] who claims, that strong acidic properties promote the formation of hydroxyacetone. The study of Suprun et al. [15] for transition metal oxides-containing aluminophosphates in the dehydration of glycerol suggests the organic nature of these new acidic sites formed during the reaction.

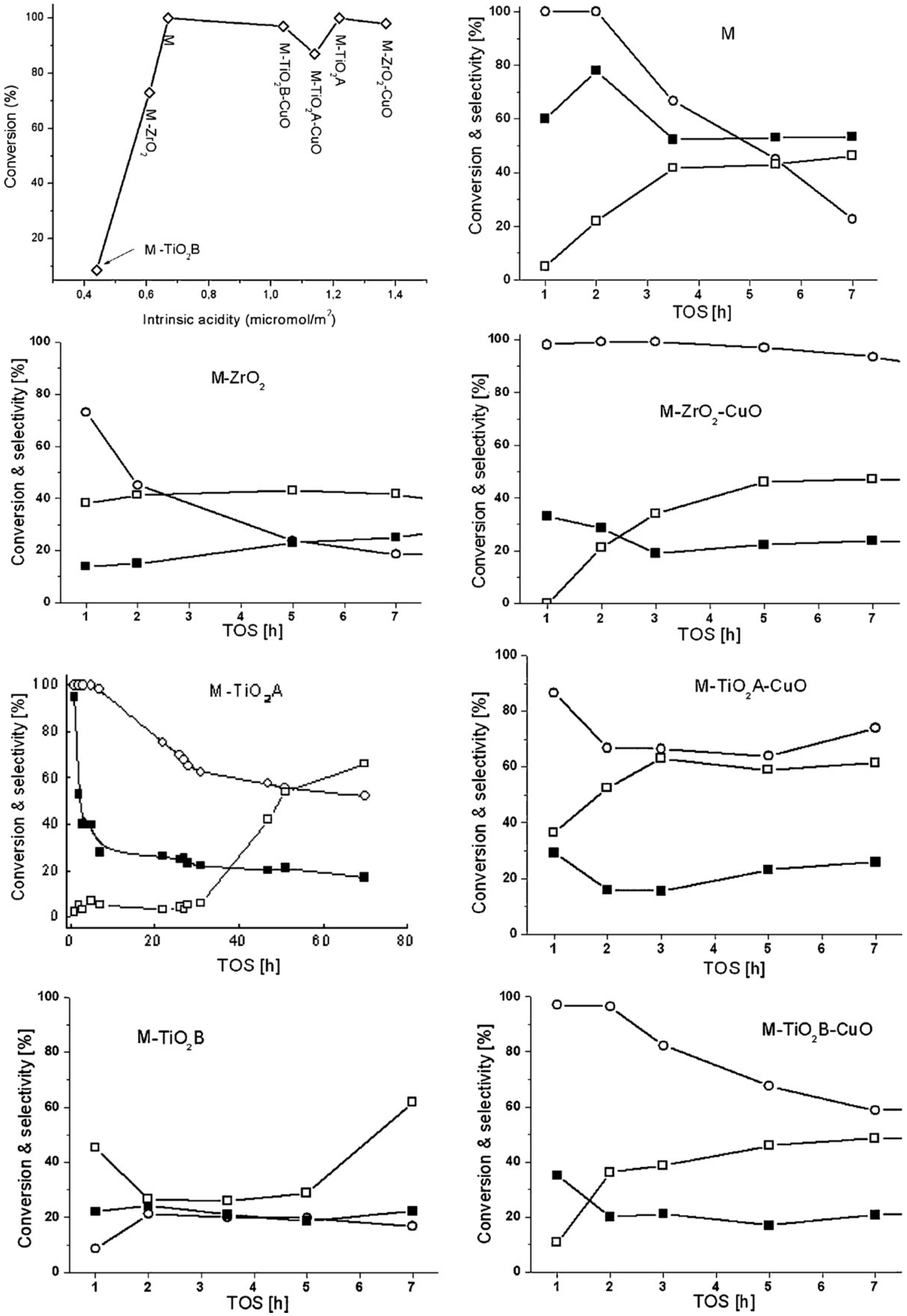

Fig. 1. (a) Dependence of the glycerol conversion on the intrinsic acidity of different catalysts. TOS: 1 h. (b)–(h) Conversion of glycerol (○) and selectivity to acrolein (■) and hydroxyacetone (□) over un-pillared, pillared and promoted montmorillonite catalysts as a function of TOS. *T*: 280 °C; GHSV: $70\,h^{-1}$.

The long-term stability test is presented in Fig. 1e. Between the 7th and 24th hour conversion decreased rapidly to ca. 60%. Then, the decrease slowed down, to ca. 50% after 72 h of reaction. Selectivity to acrolein decreased rapidly after second hour of reaction and then varied in the range of 20–30%. Hydroxyacetone, present in the small amounts at the beginning of the test, appeared in greater amounts, starting from 31st hour of the test.

These results may have their origin in the starting acidity of the samples as well as in its changes during reaction. The presence of stronger acid sites can favour the dehydration of glycerol, as suggested by Chai et al. [16]. This would explain the highest activity of M-TiO_2A, which on one hand had the highest initial acidity of the studied samples (including the highest fraction of medium–strong acidic sites), and on the other hand, formed the highest amount of the medium to strong acidic sites during the reaction.

Fig. 1a compares glycerol conversion after 1 h on stream for the studied samples as a function of intrinsic acidity. The results indicate the positive influence of intrinsic acidity of the catalyst on its activity. It was shown that higher intrinsic acidity (over 0.6 μmol NH_3/m^2 for montmorillonite catalysts) strongly increases the conversion. This is in good agreement with the literature [4,9,15,17].

Similarly as observed in [15], the studied catalysts exhibited only weak and moderate acidic sites, possibly of Lewis type. However, there is no agreement in literature about the type of acid sites necessary for the studied reaction. Chai et al. [4] claims that strong Brøensted acidity is required for selective conversion of glycerol, while other studies [5] attributed selectivity to acrolein to the presence of weak acidic sites and the absence of basic sites. This would suggest, similarly as observed in [15], that additionally to acidity, there may be other determining factors, such as redox sites, and, possibly, dispersion.

4. Conclusions

The aim of this work was to prepare and study new catalysts based on layered clays, which exhibit the set of properties required for the reaction of dehydration of glycerol: appropriate texture, as well as acidic and redox sites. From these studies it may be concluded that the structure of the supports and catalysts (texture, acidic sites, and redox sites) as well as catalytic properties were sensitive to the choice of preparation procedure. The pillaring of montmorillonite clay with TiO_2 according to the synthesis procedure A significantly increased specific surface area, acidity and the amount of easily reducible redox species, while for montmorillonites pillared with ZrO_2 and TiO_2 according to the synthesis procedure B these effects were less pronounced.

Acrolein and hydroxyacetone were the main products detected in catalytic dehydration of glycerol in presence of water. Both modification of montmorillonite structure with TiO_2 by method A or B, as well as pillaring by ZrO_2 and the impregnation with CuO had a positive influence stability of conversion. It was observed that selectivity to hydroxyacetone usually increased with time on stream. The best catalytic performance in this reaction was obtained for titania-pillared, CuO-impregnated montmorillonite, with a final selectivity to hydroxyacetone higher than 60% at 74% conversion.

Several factors were found to influence the catalytic properties. It was found that acidity plays an important role, as more acidic catalysts showed higher initial conversion and higher initial selectivity to acrolein. The presence of redox sites was found to stabilize higher conversion in later stages of the reaction and additionally changed product distribution, favouring formation of hydroxyacetone.

On the whole it may be concluded, that pillared clays promoted with CuO are promising catalysts for processing of glycerol to hydroxyacetone and to acrolein.

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