THESES OF DISSERTATION

REACTIVE DISTILLATION OF GLYCEROL USING MICRO- AND MESOPOROUS CATALYSTS

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INTRODUCTION AND THE AIM OF THE WORK

Due to the environmental policy of the European Union the use of biodiesel is growing. In the recent technologies of biodiesel production 10 wt% of glycerol is formed as by-product. It must be utilised in some fields of industry, in order to reduce the costs of biodiesel production. With arising biofuel industry, the surplus can create an oversupply of glycerol market; therefore, the price of the glycerol will drop, and it can become a waste problem in the near future. Therefore, it is necessary to convert glycerol into more valuable products.

The aim of my thesis work was to find suitable methods, catalysts, and reaction conditions to make products of high value from glycerol.

The chosen reaction was dehydration, and it was carried out by the reactive distillation method. This method allows the continuous separation of products, thus the selectivity towards intermediate products could be enhanced. This way, high amounts of acetol and acrolein could be produced, and currently they are valuable products, especially the former one.

Among the applied catalysts, there were the modified versions of the ZSM-5 zeolite, novel type of non-pyrophoric Raney-nickel varieties, and mixed oxides obtained by the calcination of layered double hydroxides (LDHs) of the hydrotalcite type.

EXPERIMENTAL

NaZSM-5 was synthesised using tetrapropylammonium bromide template. After the combustion of the template the Cr- and NiZSM5-f were prepared by conventional ion exchange. The calcined Na-containing sample was exchanged by NH_4^+; then, *via* elimination of NH_3 the HZSM-5 sample was obtained. This was used for the preparation of the Cu- and Ni-containing samples made by solid-state ion exchange. Ti-ZSM5 was prepared by isomorphic substitution.

The Raney-nickel catalysts were obtained from the inventors in order to test their properties in various reaction types. During their syntheses the aluminium content was partially dissolved by NaOH from the Ni-Al alloy under milder circumstances than the conventional methods and in some cases they were calcined as well. The samples can be considered as Al-(oxy)hydroxide supported nickel-aluminium [$NiAl{-}Ni_2Al_3/Al_xOH_y$] and Si supported nickel-silicide (NiSi), respectively.

The hydrotalcite samples were synthesised by the co-precipitation method, which means the dropwise addition of the aqueous solutions of $Al(NO_3)_3{\cdot}9H_2O+Mg(NO_3)_2{\cdot}6H_2O$ and Na_2CO_3+NaOH. The MgAl-hydrotalcite obtained was modified by the partial (10 %) exchange of Mg^{2+} and Al^{3+} to Ni^{2+}, Cu^{2+} or Cr^{3+}. The washed, filtered, and dried samples were calcined at 400 °C, 500 °C or 600 °C in order to obtain the corresponding mixed oxides.

The experimental setup for the reactive distillation consisted of a double-neck round-bottom flask equipped with a condenser, in which the products were condensed; then, trapped in a flask cooled with ice. After 120 min of reaction time, the composition of the overhead products as well as that of the distillation residue was determined. The catalyst was separated, washed and regenerated by various ways, depending on the catalyst type.

The materials tried as catalysts were characterised by X-ray diffractometry (XRD), nitrogen physisorption (BET) and thermogravimetric (TG) methods. The products formed and the distillation residue were analysed by gas chromatography (GC).

NOVEL SCIENTIFIC RESULTS

1. XRD and TG measurements verified that thermostable, crystalline H-, Ti-, Cr-, Cu- and NiZSM-5 catalysts were prepared that could be regenerated by oxidation at high temperature.

BET measurements revealed that the samples synthesized by the solid-state ion-exchange method were mesoporous, while in the other samples along with the slit-shaped mesopores, micropores could also be observed. The CuO and NiO clusters formed during solid-sate ion exchange partially blocked the channels, thus decreasing the surface area. On use, the specific surface area of the ZSM-5 samples decreased remarkably and some loss in crystallinity was observed as well. In CuZSM-5 the CuO was converted to Cu_2O, which was partially oxidised to CuO during regeneration.

2. The structure of the Raney-Ni catalyst sample did not change between 50 °C and 120 °C, but was transformed in the 120−320 °C temperature range. During reaction the intermetallic phase was separated from the various forms of Al-(oxy) hydroxides, thus the Raney structure was lost.

During heat treatment partial transformation of gibbsite, bayerite and nordstrandite to boehmite, having smaller particle size and, thus, higher specific surface area, occurred. Further increase in temperature (600 °C) converted the trihydrates and boehmite to Al_2O_3 giving even higher aluminium-nickel ratio. BET isotherms verified the presence of plate-like particles and slit-shaped mesopores in all heat-treated Raney-Ni samples. In samples heat-treated at low temperatures, micropores could be observed as well.

3. The structure of the Si- containing Raney-Ni did not change during heat treatment up to 600 ^{o}C and did not change during the dehydration reaction either, *i.e.* no phase separation occurred. This material could be regenerated by a simple calcination in air.

4. The heat-treated MgAl- and NiMgAl-LDHs produced mixed oxides were rehydrated, regaining their original lamellar structure during the dehydration reaction. Recalcination provided with the respective oxides with close to the original activities and selectivities in the repeated dehydration reaction, thus, a rehydration-recalcination regeneration method was identified.

The XRD patterns of $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$ revealed the formation of layered double hydroxide of the hydrotalcite (HT) type. The unmodified and Ni-containing samples were well-crystallised substances, while for the other samples (Cu-, Cr-, CuCr-HT) some losses in crystallinity could be observed. The layered structure collapsed on heat-treatment forming mixed oxides already at 400 °C. The incorporation of the Cu^{2+} and Cr^{3+} modifiers reduced the stability of the materials, decomposition of the samples started at lower temperature; the particle size of MgO increased lowering the specific surface area.

5. The Si-containing Raney-Ni was identified as a catalyst with high conversion and acetol selectivity, maintaining these properties after regeneration as well.

6. It has been found that the ZSM-5, the MgAl- and NiMgAl mixed oxides proved to behave as catalysts with moderate activity in the dehydration reactions of glycerol.

Over the CrZSM-5 catalysts acrolein, over HZSM-5 both acrolein and acetol, over NiZSM-5 and Ti-ZSM-5 acetaldehyde, and over CuZSM-5 acetol were the main products at moderate or low conversions. After regeneration the activities were slightly lowered and the proportion of the degradation-polymerization products was enhanced somewhat.

The MgAl and NiMgAl mixed oxide catalysts were moderately active, but they displayed high acetol selectivities.

7. Even though the Cu- and Cr-containing mixed oxide samples were highly efficient in the glycerol dehydration regarding both conversion and acetol selectivity, their original lamellar structure could not be fully restored; thus, these materials could not be regenerated.

PRACTICAL APPLICABILITY OF THE RESULTS

The topic of the theses has an importance in the field of environmental chemistry, however, the results may be considered as fundamental research. Regarding the activity, selectivity and the possibility of regeneration, the Si-containing Raney-type NiSi and the MgAl and NiMgAl mixed oxides are promising catalysts. Although some of the other samples occasionally displayed high activities and selectivities, but, unfortunately, they were transformed during the reaction; thus, they cannot be regarded as catalysts.

PUBLICATIONS RELATED TO THE THESIS

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Number of full papers
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