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The Influence of Si/Al Ratio on the Physicochemical and Catalytic Properties of MgO/ZSM-5 Catalyst in Transesterification Reaction of Rapeseed Oil

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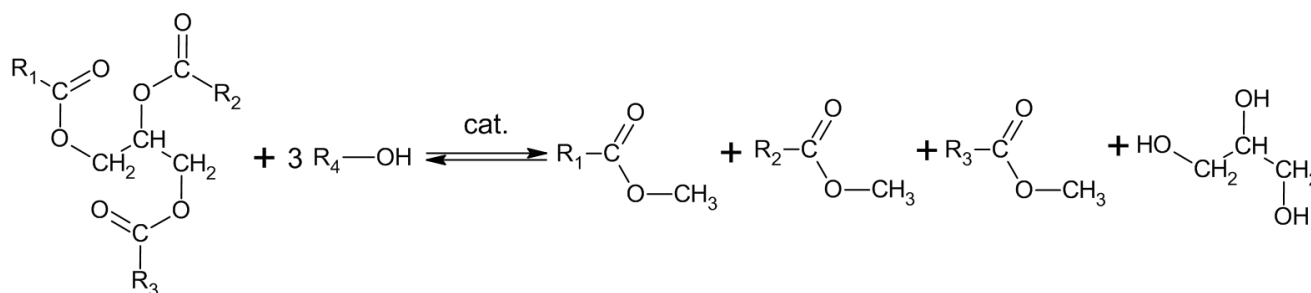
Abstract: This work presents the comparative physicochemical and catalytic studies of metal oxide MgO catalysts in a transesterification reaction. The influence of the Si/Al ratio in the catalytic material on their catalytic properties in the studied process was extensively evaluated. In addition, the effect of the type of zeolite ZSM-5 form on the catalytic reactivity of MgO based catalysts was investigated. In order to achieve the main goals of this work, a series of MgO/ZSM-5 catalysts were prepared via the impregnation method. Their physicochemical properties were studied using X-ray diffraction (XRD), BET, FTIR and TPD-CO₂ methods. The highest activity in the studied process exhibited MgO catalyst supported on ZSM-5 characterized by the highest ratio between silica and alumina. The most active catalyst system in the transesterification reaction was 10% MgO/ZSM-5 (Si/Al = 280), which showed the highest value of higher fatty acid methyl esters (94.6%) and high yield of triglyceride conversion (92.9%). The high activity of this system is explained by the alkalinity, sorption properties in relation to methanol and its high specific surface area compared to the rest of the investigated MgO based catalysts.

Keywords: ZSM-5; metal oxide catalysts; transesterification reaction; MgO; zeolite catalysts; biodiesel production

1. Introduction

The increase in the number of people along with changes in lifestyle and rapid industrialization causes a continuous increase in energy demand in recent years [1–3]. A significant part of this demand is satisfied by the consumption of natural resources, the availability of which is increasingly limited, and their constant use may eventually lead to their depletion [1]. One solution to these problems is biodiesel, which is a liquid, renewable, clean alternative fuel that has received a lot of attention due to oil depletion and environmental concerns [2,4–6]. Biodiesel has a number of advantages compared to traditional diesel fuel used in diesel engines, such as biodegradability, reduction of pollutant emissions to the atmosphere, water and soil, non-toxicity, no carcinogens, low sulfur content and low aromatic content [4,7]. Biodiesel is characterized by a high cetane number, high flash point and contains approximately 10% of oxygen-containing chemicals, which improves the complete combustion of the fuel and the quality of ignition, even in mixtures with petrodiesel [4]. Combustion of biodiesel is characterized by the reduction of emissions of carbon dioxide (CO₂), sulfur oxides (SO_x) and unburned hydrocarbons. An additional advantage is that no significant changes are required in conventional diesel engines running on biodiesel or its blends with conventional diesel fuel [3] and emit significantly less soot and carbon monoxide (CO) in the combustion gases [3,8]. Biodiesel is defined as

a mixture of long chain fatty acid methyl or ethyl esters produced by the esterification and transesterification reactions of free fatty acids (FFA) and triglycerides that naturally occur in renewable biological sources such as vegetable oils and animal fats with short-chain alcohols [9–11]. Various primary alcohols can be used in the transesterification (see Scheme 1), e.g., methanol, ethanol, propanol and butanol, which their cost is low [4]. Due to its physical and chemical nature, methanol is most often used in transesterification [10]. Natural vegetable oils without chemical modification, which, in addition to triglycerides, also contain free fatty acids have a negative feature of high viscosity and when applied directly, they can form carbon deposits and block nozzles [4,10,12].



Scheme 1. Scheme of the transesterification reaction.

In this reaction, catalysts are often introduced in order to increase the rate of reaction and ensure better efficiency of the conversion of oil to biodiesel [9]. There is a possibility of transesterification without the use of a catalyst, but it requires special conditions, such as a relatively long reaction time, high temperatures and pressures [2]. Transesterification can be carried out homogeneously or heterogeneously, with acid/base chemical catalysis, ionic liquids catalysis and enzymes bio-catalysis [4,6]. Traditional industrial methods of biodiesel production use homogeneous alkaline catalysts [6], such as alkaline hydroxides or metal alkoxides [11]. Homogeneous alkali catalysis ensures fast conversion of triglycerides from oils to biodiesel [3], with high efficiency under mild reaction conditions [6]. An additional advantage of basic catalysts can provide higher reaction rates compared to acid catalysts in the production of biodiesel [4]. The problems of alkaline homogeneous catalysis are the saponification of fatty acids and alkali cations [3], corrosion of equipment [8,13] and sensitivity to free fatty acid content of oil [14], which leads to the formation of stable emulsions and soaps [6,15]. Those type of catalysts cannot be used for high content of free fatty acid lipids in feedstock [7] and has to be anhydrous [15]. It is required to purify the obtained biodiesel through the necessary neutralization [3]. The troublesome and complex separation of products and catalysts from the final reaction mixture [3,8], which makes this process less competitive and uneconomical, and in addition it leads to a number of environmental problems related to the use of large amounts of solvents, energy [11], water for washing and wastewater, which has to be purified [15]. Typical catalysts of homogeneous acid-catalyzed transesterification are hydrochloric acid (HCl), sulfuric acid (H₂SO₄) [5], organic sulfonic acid [16], phosphoric acid [11]. The advantage of acid catalysts in transesterification is their insensitivity to free fatty acids and the water content of the oil. Acid-catalyzed reactions can be carried out under mild conditions, both in terms of temperature and pressure [14]. Besides being corrosive to reactor and equipment and difficulties of separation and purification from the liquid products, the drawbacks of homogeneous acid-catalyzed transesterification are longer time reaction than for alkaline-catalyzed reaction [17], much slower reaction rate [14], higher temperature, more waste from neutralization, difficult recycling of catalyst, weaker catalytic activity [16]. Due to the difficulties of homogeneous catalyzed transesterification, in order to avoid or minimize the problems related to homogeneous catalysis, interest in heterogeneous catalysis has been attracted [18]. The main advantage of heterogeneous catalysis is the ease of separation from the final product [2,12]. Heterogeneous alkaline catalysts are character-

ized by high possibility of reuse and regenerate the catalyst, recyclable, noncorrosive and environmentally friendly [2,16]. There are fewer disposal problems and lifetimes of this type of catalysts are longer. Heterogeneous alkaline catalysts share the same advantages as homogeneous catalysts, but also suffer from the same disadvantages, such as requirement of low FFA content in oil, requirement of anhydrous feedstock. Another demerits are requirement of higher molar ratio of alcohol to oil, high reaction temperature and pressure, diffusion limitations, poisoning of the catalyst when exposed to ambient air and high cost of synthesis. The advantages of heterogeneous acid-catalyzed transesterification are similar as for homogeneous acid-catalyzed transesterification, are insensitive to the content of FFA and water in the raw material, with a simultaneous catalysed reaction. The drawbacks of usage homogeneous acid catalysts are high cost of synthesis, which often is complicated; diffusion limitations, higher reaction temperature with a high alcohol to oil molar ratio, longer reaction time [16].

The most commonly used heterogeneous catalysts for the synthesis of biodiesel are Mg, Ca, Sr and Cs oxides, alkali hydroxides and alkali metal salts immobilized on supports and zeolites modified with K and Cs cations [19]. Zeolites are microporous aluminosilicate minerals occurring in several types [9]. Zeolites are high surface area solid acids that are characterized by homogeneous mesopores and micropores with specific pore characteristics in molecular dimensions [3,12]. Zeolites are available with different pore sizes and regulated acidity [20,21]. Their proton form is characterized by high thermal stability [20]. The acidic properties of zeolites result from the imbalance of charges between the elementary building units of zeolite, which are $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral bound in a stable, crystalline, three-dimensional, skeletal, aluminosilicate structure [3,12,22,23]. A wide variety of cations can be accommodated in the zeolite lattice, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} and many others are also found in the zeolite lattice [3,21]. Besides that, zeolites have shape selectivity [21], eco-friendliness, high size selectivity, high porosity and high surface area [4]. Zeolites are considered to be versatile catalysts due to the ability to control the basicity and the ability of ion exchange with alkali metal ions and the ability to trap metal ions or their oxides inside the micropores [13]. The acid-base properties of zeolites are controlled by the kinds and quantities of ion-exchanged cations, and by the Si/Al ratio of the main zeolite framework [24]. These properties allow the use of zeolites as selective heterogeneous catalysts, adsorbents, for the treatment and purification of water from the ion exchange beds and for humidity control [3,12]. In catalysis, more attention is paid to synthetic zeolites than to natural zeolites, due to better control of an undesired impurities and chemical composition as well as possession of optimal properties for catalytic applications. Zeolite catalysts have some disadvantages in biodiesel production in transesterification process of oils of either animal or vegetable origins, such as higher reaction temperature, longer reaction times, costly and/or complicated processes to prepare them and lower conversion efficiency compared to the process realized on homogenous catalysts. Therefore, it is essential to develop zeolite catalysts, which will be characterized by high activity and selectivity in order to reduce the cost of the produced biodiesel [9].

The main objective of this study was to determine the effect of the silicon to aluminum ratio in the MgO based catalysts. The physicochemical properties of the catalysts were studied by BET, CO_2 -TPD, FTIR and XRD methods. Based on the achieved results, the differences in the catalytic activity of these systems in the transesterification reaction of vegetable oils with methanol were explained.

2. Results and Discussion

2.1. Transesterification of Vegetable Oil with Methanol Reaction

The biodiesel production via transesterification of vegetable oil with methanol reaction was carried out at 220 °C for 2 h over zeolite supported catalysts. Magnesium oxide (MgO) was the active phase component. The prepared catalysts were calcined for 4 h in an air atmosphere at 500 °C. The activity of the reaction was expressed as triglycerides (TG) conversion values and fatty acids methyl esters (FAME) yield. The reaction was

performed in an autoclave with continuous stirring of the reaction mixture. Each process was performed for 2 h in order to obtain the final product of a mixture of the fatty acid alkyl esters, known as biodiesel. The obtained results in the studied process were presented in Table 1 and Figures 1 and 2, respectively. The catalytic activity tests carried out in the biodiesel production process showed that all prepared catalysts exhibited a very high TG conversion with a high FAME yield (see Figures 1 and 2). The lowest TG conversion (88.9%) and efficiency to FAME (79.3%) was demonstrated by the 10% MgO/Al₂O₃ catalyst. A similar triglyceride conversion was exhibited by catalysts loaded onto the hydrogen form of ZSM-5 zeolites derived from heating the ammonium form of the NH₄-ZSM-5 zeolite at 500 °C for 15 h, but this system demonstrated a higher FAME yield. The results of the activity tests show that the increase of the silicon to aluminum ratio in the zeolite support has a positive effect on triglycerides conversion and yield of FAME production (see Figures 1 and 2).

Table 1. The results of the transesterification process performed over various MgO catalysts, calcined systems. The ratio of silicon to aluminum is given in parentheses. Mean values and standard deviations (in parentheses) of triglyceride conversions and FAME yields are given in the table.

Catalyst	Reaction Temperature (°C)	Reaction Time (h)	Molar Ratio Methanol: Oil	Calcination Temperature (°C)	Catalyst Weight (g)	Triglycerides Conversion (%)	FAME Yield (%)
10% MgO/Al ₂ O ₃	220	2	9:1	500	0.5	88.9 (0.7)	79.3 (1.5)
10% MgO/ZSM-5 (23)	220	2	9:1	500	0.5	92.7 (0.8)	86.1 (0.8)
10% MgO/ZSM-5 (50)	220	2	9:1	500	0.5	94.0 (1.3)	92.0 (0.6)
10% MgO/ZSM-5 (280)	220	2	9:1	500	0.5	92.9 (0.7)	94.6 (1.0)
10% MgO/SiO ₂	220	2	9:1	500	0.5	94.0 (0.6)	83.3 (0.6)
10% MgO/HZSM-5 (50)	220	2	9:1	500	0.5	88.9 (0.5)	81.7 (1.5)
10% MgO/HZSM-5 (280)	220	2	9:1	500	0.5	89.0 (1.0)	86.0 (1.5)

Furthermore, there are differences in catalytic activity between the catalysts impregnated onto the hydrogen form of ZSM-5 zeolites and the catalysts impregnated directly onto the NH₄-ZSM-5 zeolite. For the catalysts on the HZSM-5 support, the TG conversion is lower by about 5%, while the FAME yield decreased by about 8–10%, in comparison to the catalysts impregnated on the NH₄-ZSM-5 form of zeolite. This implies that no prior calcination of the zeolite support is needed to achieve high activity in the tested process. The catalytic system having the highest activity was the one containing 10% MgO/ZSM-5 (Si/Al = 280). This catalyst exhibited the highest value of FAME yield of 94.6% with the second highest triglyceride conversion (92.9%). This catalytic system, due to its high activity and high selectivity makes it considerable to use for testing it on an industrial scale.

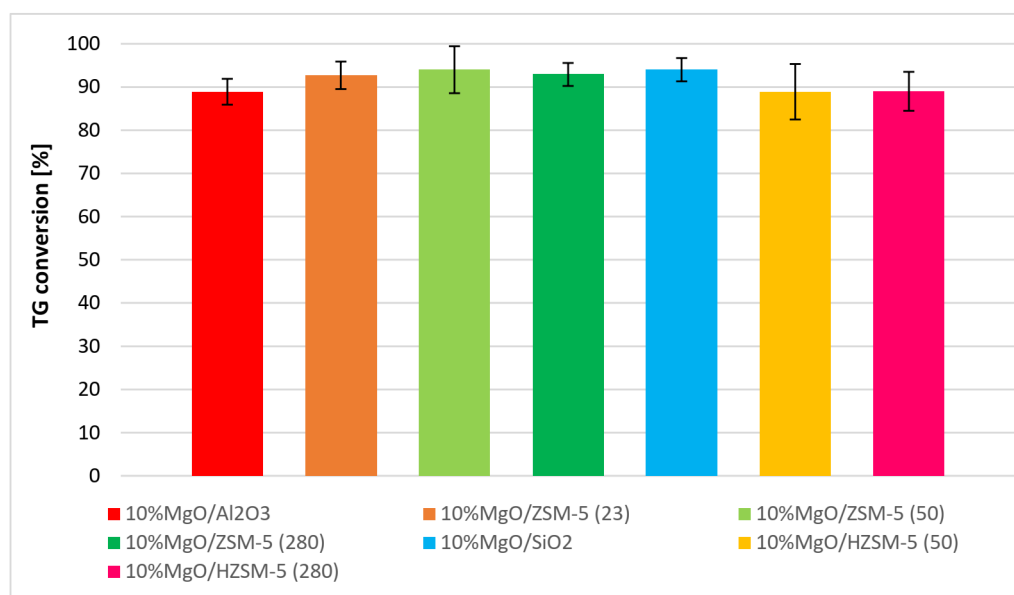


Figure 1. TG conversion obtained for the investigated MgO based catalysts. The ratio of silicon to aluminum is given in parentheses.

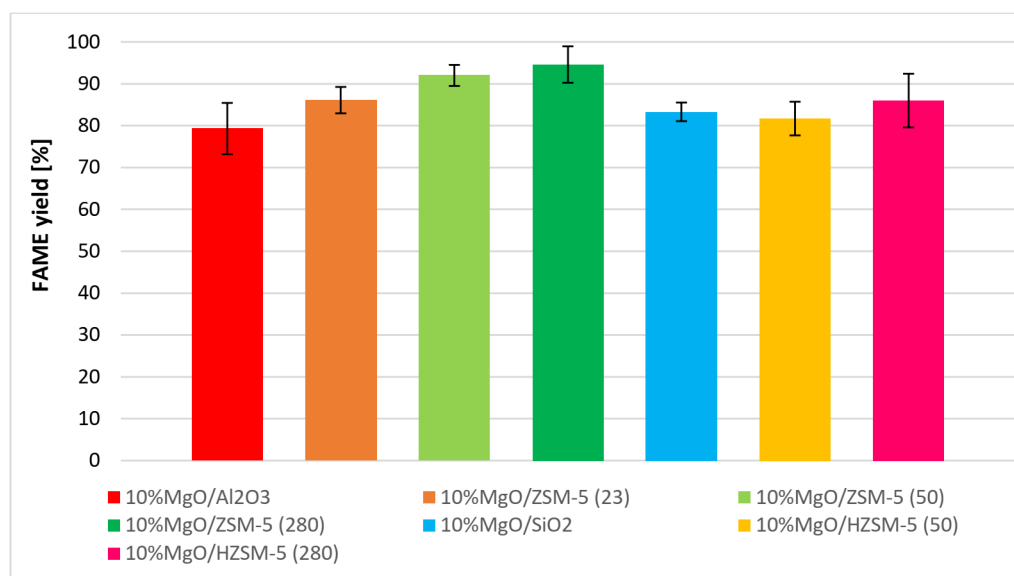


Figure 2. FAME yields obtained for the investigated MgO based catalytic systems. The ratio of silicon to aluminum is given in parentheses.

Qu et al. [25] investigated MgO/ZSM-5 catalysts synthesized via impregnation and ultrasonic dispersion methods in the transesterification of *Spirulina platensis* algae oil with ethanol. The authors achieved 92.1% yield of biodiesel after 1 h reaction at 75 °C with 3 wt.% of catalyst concentration and an alcohol-to-oil ratio of 15:1. The ZSM-5 zeolite was activated with NaOH and dried at 600 °C for 6 h in a muffle furnace with the calcination. In another article, Qu et al. [26] investigated the microwave-assisted in-situ transesterification of *Spirulina platensis* algae oil with PEG/MgO/ZSM-5@Fe₃O₄ magnetic catalysts synthesized using polyethylene glycol (PEG) as a mediator. The transesterification reaction was carried out in a flask, which was placed in a microwave reactor. Before the reaction, the catalysts were calcined at 650 °C in a nitrogen atmosphere for 4 h. The authors obtained the highest biodiesel yield of 95.8% for a reaction temperature of 70 °C, a reaction time of 40 min, an ethanol/biomass mass ratio of 8:1, using a 2 wt% catalyst in which the weight percentage of PEG was 15 wt% (15PEG/MgO/ZSM-5@Fe₃O₄). Li and Rudolph [27] introduced MgO

into MCM-41, SBA-15, and KIT-6. All catalysts were synthesized by impregnation and by in situ coating. Prepared catalysts were applied to transesterification of commercial-edible-grade blended vegetable oil with ethanol in a batch reactor under continuous stirring. The most effective catalyst was found to be SBA-15 impregnated with MgO, achieving a high conversion of 96% in a reaction carried out at 220 °C for 5 h. The activity of the studied zeolites can be improved by controlling the physicochemical properties through the dealumination process in various processes, not only in the biodiesel production process via transesterification of the vegetable oil and methanol. Sithole et al. [28] prepared MgO/Al₂O₃ catalysts for biodiesel production with waste vegetable oils as a feedstock. The oil conversion of 95% was achieved for 20% MgO/Al₂O₃ catalyst for the reaction carried out at 225 °C, for 60 min, with a methanol to oil ratio of 18:1 using 3 wt.% of catalyst. Mohadesi et al. [29] investigated alkaline earth metal oxides (MgO, CaO and BaO) supported on silica in transesterification of refined corn oil with methanol. All experiments were performed in 250mL two-necked flask equipped with a thermometer and a condenser and the reaction mixture with catalyst was stirred at 600 rpm at 60 °C for 8 h with the molar ratio of oil-to alcohol of 1:16. The amount of used catalyst was 6 wt%. Methyl ester content in the final product of reaction with 60%MgO/SiO₂ catalyst calcined at 650 °C for 3 h was 81.4%.

In order to verify the amount of MgO in the studied catalysts supported on ZSM-5 zeolites and to find out whether small differences in magnesium oxide content could be important to justify the reactivity results observed for investigated materials in the transesterification process, the catalytic material samples were measured by FAAS technique. The obtained results are shown in Table 2.

Table 2. The content of MgO in the investigated calcined catalytic systems.

Material	MgO Content (%)
10% MgO/ZSM-5 (Si/Al = 23)	9.7779
10% MgO/ZSM-5 (Si/Al = 50)	9.3104
10% MgO/ZSM-5 (Si/Al = 280)	8.6448
10% MgO/HZSM-5 (Si/Al = 50)	9.2732
10% MgO/HZSM-5 (Si/Al = 280)	8.9759

The calculated MgO loading for the catalysts supported on ZSM-5 zeolites was 10%. The highest amount of magnesium oxide (9.7779%) was determined by the FAAS technique for the 10% MgO/ZSM-5 (Si/Al = 23) catalyst, which was directly impregnated on the ammonium form of ZSM-5 zeolite and exhibited the lowest TG conversion (92.7%) and the lowest FAME yield (86.1%) compared to the rest of the catalytic materials synthesized the same way, while the lowest amount of magnesium oxide (8.6448%) was detected for the 10% MgO/ZSM-5 (Si/Al = 280) catalyst, which exhibited similar TG conversion (92.9%), but the highest FAME yield (94.6%). Lower magnesium oxide content was found for catalysts impregnated directly onto ammonium forms of support characterized by a higher silicon to aluminum ratio. In the case of the magnesium oxide catalyst supported on the hydrogen form of ZSM-5 zeolite, higher MgO content (9.2732%) is found for 10% MgO/HZSM-5 (Si/Al = 50) catalyst. While FAAS analysis performed for the 10% MgO/HZSM-5 (Si/Al = 280) catalyst showed 8.9759% wt. of MgO. The conversion of triglycerides and FAME yield exhibited by MgO catalysts supported on HZSM-5 in the transesterification reaction of rapeseed oil with methanol were lower than for catalysts directly impregnated on NH₄-ZSM-5 zeolite.

Theoretically, the higher content of MgO as the active phase in the supported catalysts should improve the activity, due to the higher number of active centers. However, the obtained activity results suggest that the reactivity of the studied systems may be affected by the properties of the support i.e., acid-base properties, specific surface area. Another possible explanation for the observed differences in the catalytic activity of the different systems could be the higher dispersion of active phase and/or better availability of active

sites for the reactants in the systems where a lower MgO content was determined by the FAAS technique. This could result in higher TG conversions and FAME yields.

2.2. Specific Surface Area Measurements of the Catalytic Materials

The specific surface area (SSA) measurements were done for MgO catalysts using the N₂ adsorption–desorption method. All values of the specific surface area, pore volume and average pore radius are presented in Table 3 for the selected MgO catalysts. The SSA results clearly shows that the MgO catalysts supported on monooxide Al₂O₃ and SiO₂ were characterized by the lowest SSA values equal 122.81 and 203.44 m²/g, respectively. The highest SSA had 10% MgO/HZSM-5 (Si/Al = 280) catalysts and it exhibited the lowest average pore radius compared to the rest of the investigated catalysts systems. The obtained results presented in Table 3 show that the increasing Si/Al ratio in the catalytic system results in an increase of the SSA for both NH₄-ZSM-5 and HZSM-5 forms of the zeolites. It is also worth mentioning that the MgO catalysts supported on both forms of zeolites characterized by the highest ratio between Si/Al exhibited higher catalytic activity in the biodiesel production process compared to the rest of the investigated catalysts.

Table 3. The specific surface area, pore volume and average pore radius for MgO catalysts supported on various carriers.

Materials	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Radius (nm)
10% MgO/Al ₂ O ₃	122.81	0.18	6.02
10% MgO/ZSM-5 (Si/Al = 50)	259.78	0.22	3.34
10% MgO/ZSM-5 (Si/Al = 280)	278.40	0.17	2.44
10% MgO/HZSM-5 (Si/Al = 50)	244.33	0.20	3.27
10% MgO/HZSM-5 (Si/Al = 280)	307.24	0.19	2.49
10% MgO/SiO ₂	203.44	0.93	18.23

2.3. Phase Composition Studies of Catalysts

The XRD analysis was performed and also used to determine the phase composition studies of the magnesium oxides supported zeolite catalysts after their calcination process. The analysis of these measurements were given in Figure 3. Analyses of the diffraction patterns of the calcined magnesium oxide catalysts showed the respective diffraction peaks for the relevant catalysts. The characteristic diffraction peaks for magnesium oxide (MgO) are visible at $2\theta = 30.92^\circ, 35.08^\circ, 35.77^\circ, 36.87^\circ, 42.88^\circ, 62.38^\circ, 74.81^\circ$ and 78.75° . Zhou Shijian et al. [30] in their work used MgO-Al₂O₃/ZSM-5 catalysts synthesized in a solid state reaction for the dehydrogenation of propane. On the XRD patterns, they observed MgO species at angle values of $2\theta = 43^\circ$ and 62° , confirming the presence of MgO on the zeolite surface. Shaheen et al. [31], in their work, investigated among others MgO nanocatalyst in the conversion of Silybum eburneum seed oil to liquid biodiesel. On the X-ray diffractogram, they identified three reflexes attributed to MgO at $2\theta = 36.8^\circ, 42.8^\circ$ and 62.1° , which correspond to (111), (200) and (220), respectively. The latter diffraction MgO peaks are corresponding to (004) for $2\theta \approx 31^\circ$; (311)—for $2\theta \approx 75^\circ$ and (222) for $2\theta \approx 78^\circ$, respectively [32]. The rest of the diffraction peaks visible on the XRD patterns of the tested catalysts originated from the ZSM-5 zeolites (with the following 2θ angle values: $7.91^\circ, 8.84^\circ, 10.94^\circ, 11.85^\circ, 13.14^\circ, 13.85^\circ, 14.70^\circ, 15.46^\circ, 15.86^\circ, 16.45^\circ, 17.18^\circ, 17.73^\circ, 18.62^\circ, 19.15^\circ, 19.43^\circ, 19.68^\circ, 20.26^\circ, 20.76^\circ, 21.64^\circ, 22.07^\circ, 22.43^\circ, 22.96^\circ, 23.61^\circ, 23.80^\circ, 24.65^\circ, 25.44^\circ, 25.77^\circ, 26.45^\circ, 26.82^\circ, 27.38^\circ, 27.91^\circ, 28.29^\circ, 29.14^\circ, 29.90^\circ, 30.23^\circ, 31.07^\circ, 32.01^\circ, 32.60^\circ, 33.23^\circ, 34.22^\circ, 34.95^\circ, 35.52^\circ, 36.21^\circ, 37.26^\circ, 38.57^\circ, 40.79^\circ, 41.16^\circ$ and 43.26°). All the MgO catalyst samples supported on the ZSM-5 zeolites display sharp intensity peaks on the XRD patterns, which can be considered good preservation of the ZSM-5 zeolite

structure during sample preparation [30]. An analysis of the diffraction curve of 10% MgO/SiO₂ catalyst shows that this sample is a completely amorphous system. The pattern presents only a broad diffraction peak with a value of 2θ angle equals 23.00° assigned to the silica crystallographic phase. Unfortunately, the amorphosity of 10% MgO/SiO₂ catalyst did not allow the crystallite size to be determined from the XRD data obtained using the Scherrer equation. The XRD diffraction curve recorded for the 10% MgO/Al₂O₃ catalyst showed slightly better crystallinity compared to the MgO catalyst supported on silica. The XRD pattern of this system shows diffraction peaks with values of 2θ = 19.51°, 32.30°, 37.18°, 45.50° and 67.09° attributed to the γ -Al₂O₃ [33]. Boz et al. [34] identified that diffraction peaks at 2θ = 37.0°, 46.0° and 67.0° correspond to the γ -Al₂O₃ polymorphic form. There are also visible reflexes on the pattern derived from MgO at 2θ = 42.88°, 62.38°.

In addition, the phase analysis of all the prepared catalysts, the crystallite size of the active phase in the studied systems was also investigated by calculating the crystallite size of MgO based on the Scherrer equation [33]:

$$D_{hkl} = k\lambda / \beta \cos\theta, \quad (1)$$

where D is the mean dimension of the crystallite perpendicular to the plane (hkl); β is the integral, full widths at half maximum (FWHM) in radians; $k = 0.89$ is a constant dependent on the crystallite shape, and λ is the X-ray wavelength. The diffraction patterns were processed using HighScore Plus software by fitting to pseudo-Voigt function. Determining the size of the crystallites was quite difficult due to the large number of peaks originating from ZSM-5 zeolites and low crystallinity for the catalysts supported on alumina. The results of the calculation performed for the calcined catalysts are given in Table 4. The lowest size of magnesium oxide crystallites was observed for 10% MgO/ZSM-5 calcined catalyst (Si/Al = 23). This catalyst exhibited high TG conversion and FAME yield, however, the obtained activity results were not the best. For the catalytic systems supported on ZSM-5 zeolite supports featuring silicon/alumina ratios of 50 and 280, the size of MgO crystallites increased.

2.4. Basic Properties of the Synthesized Catalyst Systems

The CO₂-TPD experiments were used to characterize catalytic materials' alkalinity and the results are shown in Table 5. All the catalytic materials were previously heated at 600 °C before a proper alkalinity test. The results show that all the catalysts exhibited three types of desorption centers with various strengths (weak, medium and strong) and mainly have weak desorption centers (100–300 °C). The sum of the basicity values of all materials indicates that the material with the highest alkalinity was a 10% MgO/HZSM-5 (Si/Al = 50) catalyst (0.75 mmol/g), while the 10% MgO/SiO₂ catalyst has the lowest alkalinity (0.35 mmol/g). In general, as the amount of silicon to aluminum in the catalyst support increases, a decrease in the basicity of the catalyst system is observed. A significant increase in alkalinity is seen for the catalyst loaded on the hydrogen form of the zeolite ZSM-5 (Si/Al = 50) compared to the catalyst loaded on the ammonium form of ZSM-5, while the difference in alkalinity between the MgO systems loaded on HZSM-5 (Si/Al = 280) and NH₄-ZSM-5 (Si/Al = 280) is negligible. The oxygen-related base sites in the occurring pairs Mg²⁺-O²⁻ and Al³⁺-O²⁻ are responsible for CO₂ desorption at about 200 °C. Desorption in the temperature range of 250–300 °C can be attributed to stronger basic sites corresponding to isolated O²⁻ anions, while desorption at temperatures above 350 °C is attributed to corresponding isolated O²⁻ but localized at a specific surface site [35].

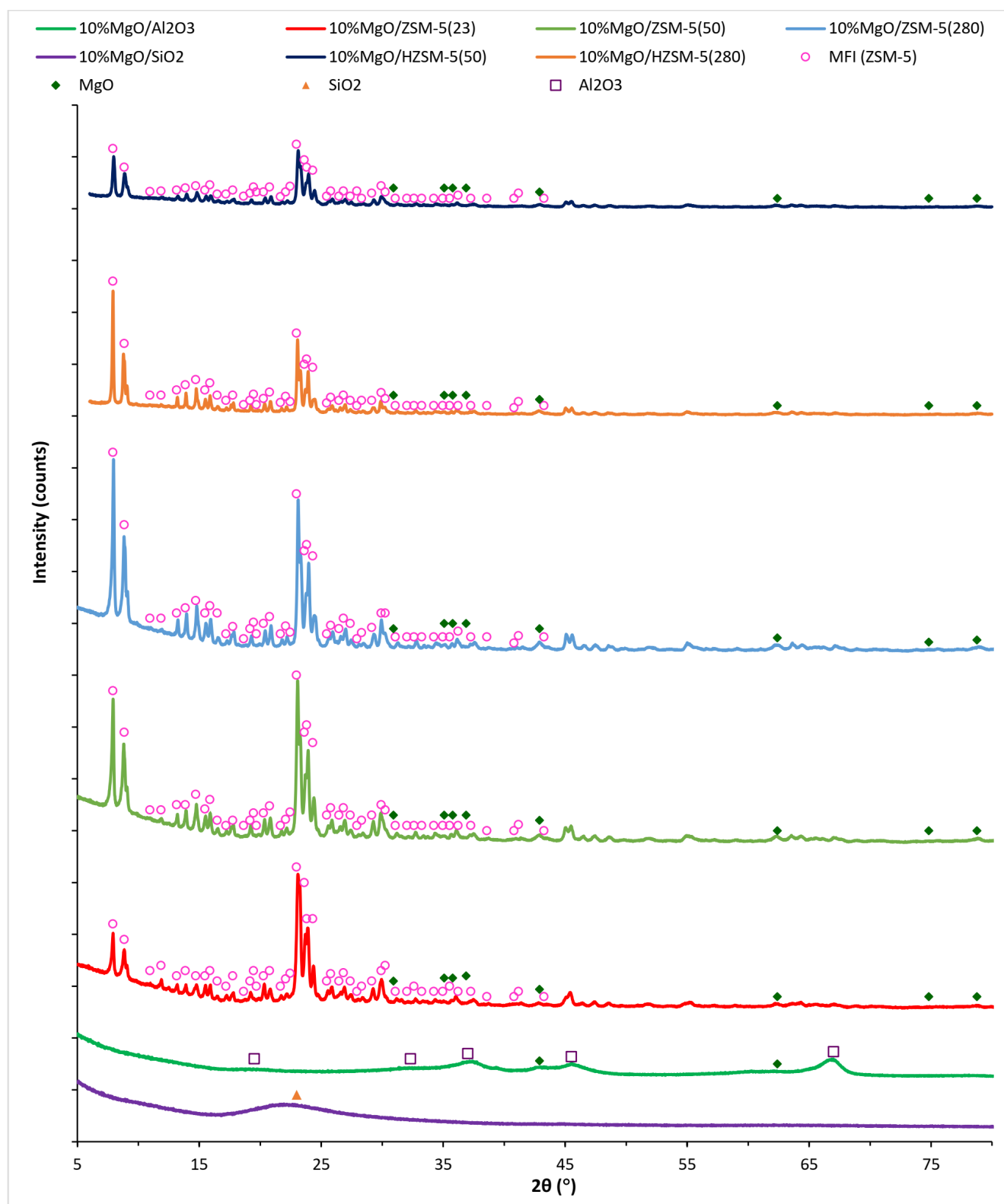


Figure 3. XRD diffraction curves of the calcined 10% MgO/Al₂O₃, 10% MgO/SiO₂, 10% MgO/ZSM-5 and 10% MgO/HZSM-5 catalysts in an air atmosphere at 500 °C for 4 h. The ratio of silicon to aluminum is given in parentheses.

Table 4. Crystallite size of the active phase (MgO) of catalysts supported on ZSM-5 zeolite and oxide supports calculated from XRD data using Scherrer equation.

Catalyst	MgO Crystallite Size (nm)
10% MgO/Al ₂ O ₃	16
10% MgO/ZSM-5 (Si/Al = 23)	8
10% MgO/ZSM-5 (Si/Al = 50)	10
10% MgO/ZSM-5 (Si/Al = 280)	15
10% MgO/SiO ₂	***
10% MgO/HZSM-5 (Si/Al = 50)	17
10% MgO/HZSM-5 (Si/Al = 280)	15

*** due to amorphosity of the sample, it was not possible to determine the crystallite size of the magnesium oxide.

Table 5. The amount of CO₂ adsorbed on the support surface (calcined in an air atmosphere for 4 h at 500 °C), magnesium oxides catalysts supported on ZSM-5 zeolite with a different silicon to aluminum ratio, calculated from the CO₂-TPD profiles. The ratio of silicon to aluminum is given in parentheses.

Catalytic Systems	Weak Centers (mmol/g) 100–300 °C	Medium Centers (mmol/g) 300–450 °C	Strong Centers (mmol/g) 450–600 °C	Total Basicity (mmol/g) 100–600 °C
10% MgO/Al ₂ O ₃	0.31	0.15	0.11	0.57
10% MgO/ZSM-5 (23)	0.22	0.17	0.13	0.51
10% MgO/ZSM-5 (50)	0.16	0.23	0.10	0.49
10% MgO/ZSM-5 (280)	0.27	0.10	0.08	0.46
10% MgO/SiO ₂	0.17	0.10	0.08	0.35
10% MgO/HZSM-5 (50)	0.42	0.22	0.05	0.69
10% MgO/HZSM-5 (280)	0.27	0.12	0.09	0.48

2.5. Sorption Properties of Magnesium Oxide Catalysts Supported on ZSM-5 Zeolites in Relation to Methanol

The next stage of physicochemical studies conducted on the synthesized catalytic systems investigated the sorption properties of MgO catalysts supported on ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios calcined at 500 °C in an air atmosphere for 4 h with the methanol-argon mixture. In addition to this, MgO/Al₂O₃, MgO/SiO₂ and MgO/HZSM-5 systems, which were prepared and calcined in an air atmosphere for 4 h at 500 °C for comparison, were also investigated. The purpose of this study was to clarify and understand the activity of the studied systems in the biodiesel production process. The results of FTIR studies are shown in Figure 4. Several characteristic IR bands can be easily distinguished in the spectra recorded for the studied catalysts. The bands seen in the FTIR spectra above 3250 cm^{−1} for the MgO catalysts supported on ZSM-5 zeolites correspond to the assigned OH stretching [36]. All the catalysts in the IR spectra show specific bands in the region 2956–2948 cm^{−1}, which are attributed to (ν_{asym}(CH₃)) antisymmetric CH stretching vibrations and in the region 2859–2832 cm^{−1}, which corresponds to (ν_{sym}(CH₃)) symmetric CH stretching vibrations from methoxy groups [37,38]. It should be emphasized that the highest intensity of these bands was observed for the 10% MgO/ZSM-5(23) system, which confirms the strongest adsorption of methanol on the catalyst surface compared to the other studied catalysts. On the other hand, the intensity of these bands is smaller for the 10% MgO/ZSM-5(50) and 10% MgO/ZSM-5(280) catalysts. This result indicates that increasing the silicon to aluminum ratio in the catalytic system reduces the sorption properties of the catalytic system in relation to methanol. The FTIR analysis performed for the catalysts supported on hydrogen form of the HZSM-5(50) zeolite showed similar bands on the IR spectrum as for the corresponding catalyst impregnated directly onto the ammonium form of the ZSM-5 zeolite. While the IR bands located in the spectrum of 10% MgO/HZSM-5(280) are much more intense than those recorded for 10% MgO/ZSM-5(280) catalyst. Whereas the FTIR measurements performed for 10% MgO/HZSM-5(50), 10%

MgO/HZSM-5(280), 10% MgO/ZSM-5(23) and 10% MgO/ZSM-5(50) catalysts confirmed the occurrence of additional weak IR bands located in the range $1927\text{--}1991\text{ cm}^{-1}$ on the FTIR spectrum which are corresponding to a shift of the Si-O combination bands of the adsorbent. In addition, the spectra recorded for all catalysts, with the exception of the 10% MgO/ZSM-5(23) catalyst, show strong bands located at the value of $1576\text{--}1589\text{ cm}^{-1}$, which are characterized by deformation vibrations occurring in -OH species [36]. The negative band above 1600 cm^{-1} that appears on the FTIR spectra is most likely due to the removal of initially adsorbed water ($\delta(\text{OH})$) [39]. The intense negative bands seen in the wavenumber range of $1200\text{--}1331\text{ cm}^{-1}$ can be attributed to the $\delta(\text{OH})$ modes of H-bonded zeolite hydroxyls [39].

Furthermore, FTIR measurements carried out for all investigated catalysts allow the conclusion that the greatest quantity of adsorbed methanol was observed for 10% MgO/ZSM-5(23) catalyst calcined in an air atmosphere for 4 h at $500\text{ }^{\circ}\text{C}$. The obtained FTIR spectra recorded for all studied systems indicate that the quantity of methoxide species adsorbed on the catalyst surface is one of the first steps of the transesterification process over the catalyst surface and plays an important role during the investigated reaction using the synthesized catalyst systems. Correlating the obtained experimental results with the catalytic activity for the tested systems, it can be concluded that for catalysts impregnated on various types of $\text{NH}_4\text{-ZSM-5}$ zeolites, the adsorption of methanol depends on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, and weaker adsorption improves the FAME yield.

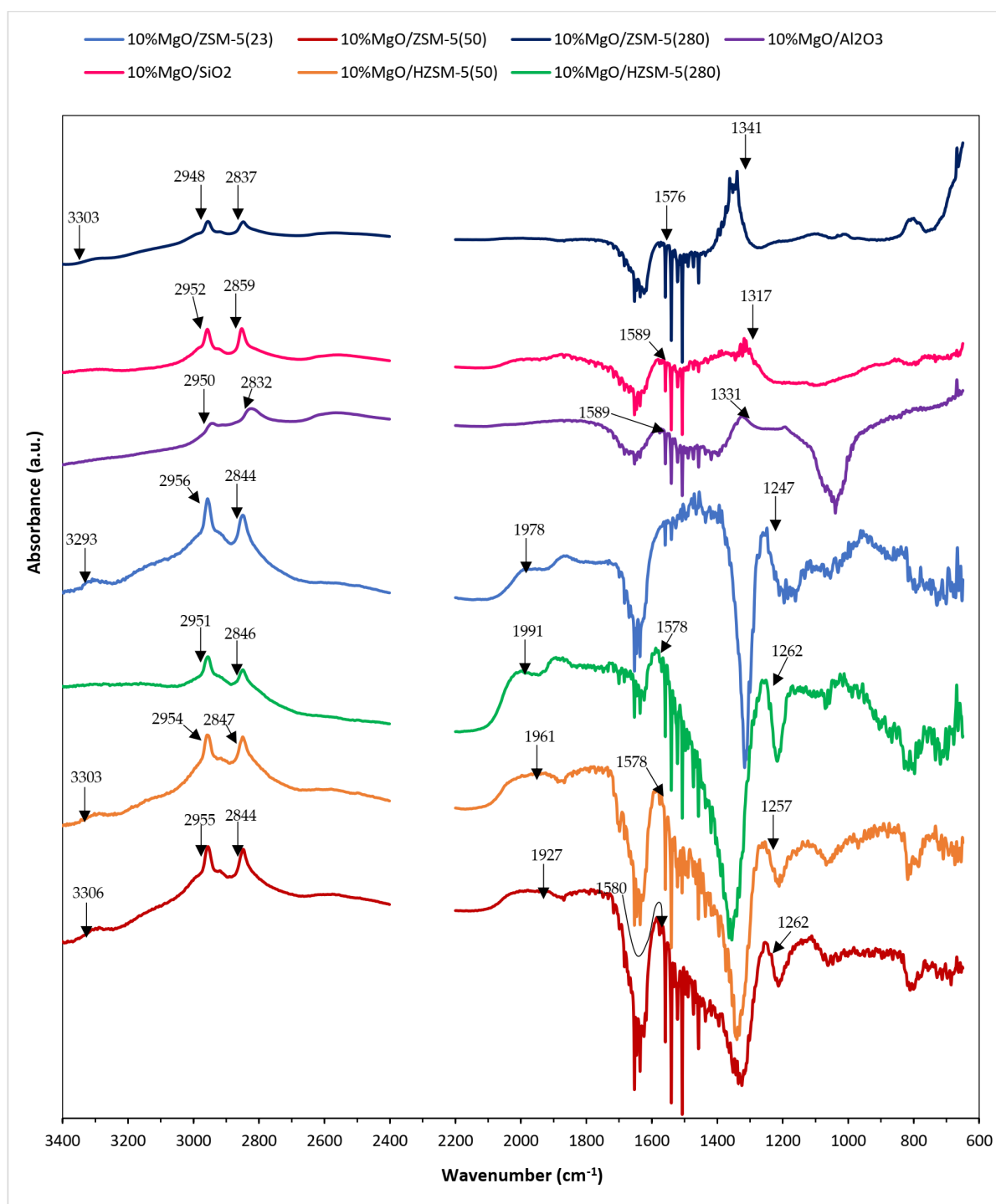


Figure 4. FTIR difference spectra of adsorbed species taken after exposure of the catalytic system (10% MgO/Al₂O₃, 10% MgO/SiO₂, 10% MgO/ZSM-5 and 10% MgO/HZSM-5) calcined in an air atmosphere at 500 °C for 4 h, to a mixture of 6 vol% methanol–94% argon mixture at 50 °C and after the evacuation of this mixture for 10 min using argon stream. The ratio of silicon to aluminum is given in parentheses.

3. Materials and Methods

3.1. Preparation of the Catalytic Materials

Magnesium oxide catalysts were synthesized by impregnation method using zeolite ZSM-5 as a support. The ammonium form NH₄-ZSM-5 zeolite with different silicon to aluminum ratios of 23, 50, and 280, respectively, was used in this study and all zeolites were

purchased from Zeolyst International (Kansas City, KS, USA). A part of the ZSM-5 zeolites with silicon to aluminum ratios of 50 and 280, respectively, was converted to the hydrogen form (HZSM-5) by calcination for 15 h in an air atmosphere at 500 °C. $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (Sigma Aldrich, ACS reagent, St. Louis, MO, USA) was used as the precursor of the active phase component. The support was impregnated with an aqueous precursor salt, and the impregnation time was 24 h. The amount of aqueous precursor salt solution used during the impregnation step for each catalyst was 150 mL. The loading of the MgO catalysts was 10% wt. [40]. Magnesium oxide catalysts supported on commercial oxide supports—alumina or silica—were also synthesized for comparison purposes. All catalysts were evaporated on a rotary evaporator and calcined in an air atmosphere for 4 h at 500 °C.

3.2. Characterization of the Catalytic Material

The phase composition studies of supports and catalysts were investigated using the X-ray diffraction technique (XRD). X-ray diffraction patterns were recorded on a PANalytical X'PertPro MPD diffractometer in Bragg–Brentano reflecting geometry (Malvern Panalytical Ltd., Malvern, UK). $\text{Cu K}\alpha$ radiation ($\lambda = 154.05 \text{ pm}$) from a sealed tube was used in the 2θ angle range 5–90°. The TPD- CO_2 measurements were performed in a quartz microreactor using CO_2 as a probe molecule. The CO_2 was adsorbed on the catalyst surface at 50 °C for 30 min after drying in flowing helium at 500 °C for 60 min. TPD- CO_2 measurements were carried out in the temperature range 100–600 °C, after removing physisorbed CO_2 from the catalyst surface. FTIR measurements were done using a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific Co., Waltham, MA, USA) equipped with a liquid-nitrogen cooled MCT detector. A resolution of 4.0 cm^{-1} was used throughout the investigation. A total of 64 scans were taken to achieve a satisfactory signal-to-noise ratio. The background spectrum was collected at 50 °C in an argon stream. Before the measurements, argon was shifted to a mixture of 6 vol % CH_3OH in the argon stream. The adsorption process involved exposure of the heated catalysts to 6 vol % CH_3OH in an argon stream flowing at $40 \text{ cm}^3/\text{min}$ for 10 min under atmospheric pressure. After the adsorption process, the cell was evacuated for 15 min in an argon stream, and then the spectrum was collected. FTIR spectra of adsorbed species were taken after exposure of the catalysts (10% $\text{MgO}/\text{Al}_2\text{O}_3$, 10% $\text{MgO}/\text{ZSM-5}$ (Si/Al = 23), 10% $\text{MgO}/\text{ZSM-5}$ (Si/Al = 50), 10% $\text{MgO}/\text{ZSM-5}$ (Si/Al = 280), 10% $\text{MgO}/\text{HZSM-5}$ (Si/Al = 50), 10% $\text{MgO}/\text{HZSM-5}$ (Si/Al = 280), 10% MgO/SiO_2) calcined in an air atmosphere at 500 °C for 4 h, to a mixture of 6 vol % methanol–94% argon mixture at 50 °C and after the evacuation of this mixture for 15 min using an argon stream. The collected FTIR spectra were recorded in transmittance mode, which were converted to absorbance mode and subtracted from the previously collected background of the bare catalyst. Magnesium concentration in the prepared catalysts was determined by flame atomic absorption spectrometry (acetylene/air) at a wavelength of 285.2 nm on a SOLAAR M6 (Unicam Atomic Absorption, Cambridge, UK) spectrometer equipped with an HCL hollow cathode lamp for magnesium determination and a nebulizer with a platinum-iridium capillary, allowing sample aspiration at a rate of 6 mL/min. The spectral width of the slit was 0.5 nm. The gas flow rate was 0.9 L/min and the height of the burner was 14.2 mm. Approximately 0.1 g of the analyzed 10% $\text{MgO}/\text{zeolite}$ catalyst sample was weighed on an analytical balance into disposable Teflon vessels, followed by the addition of 2 mL of 65% HNO_3 and 4 mL of HF. Then, the samples were pre-mineralized at 25 °C for 25 min in an ultrasonic bath (BANDELIN, Berlin, Germany). Next, the samples were mineralized in a closed UltraWave microwave system (Milestone, Italy) according to the procedure shown in Table 6. The dissolved samples were transferred to 25 mL volumetric flasks and filled with deionized water.

Table 6. Sample mineralization conditions.

Step	Time (min)	T_1 (°C)	T_2 (°C)	Pressure (bar)	Power (W)
1	25	240	70	110	1500
2	10	240	70	110	1500

3.3. Catalytic Activity Measurements in Transesterification of the Vegetable Oil with Methanol

The transesterification process was carried out in an autoclave using a substrate mixture of rapeseed oil and CH₃OH with a molar ratio of 9:1. In this reaction, commercial rapeseed oil was used. Methanol used in this reaction was purchased from CHEMPUR, Piekary Śląskie, Poland. In all catalytic tests, a weight of about 0.5 g was used. The reaction was performed at 220 °C for 2 h. Before reaction tests, catalysts were calcined at 500 °C for 4 h. The obtained reaction products were analyzed by the HPLC technique (Shimadzu, Kyoto, Kyoto Prefecture, Japan). In all catalytic tests, column C-18 (5 µm, 4.6 × 250) and a mixture of 2-isopropanol-hexane (4:5) and methanol was used as eluent, all chemicals were purchased from CHEMPUR, Piekary Śląskie, Poland. The mobile phase gradient applied during each experiment was shown in Table 7. The products of the reaction were analyzed using a DAD detector (wavelength: λ = 205 nm) (Shimadzu, Kyoto, Kyoto Prefecture, Japan) to define the triglycerides conversion and to identify of FAME yield.

Table 7. Phase gradient used in the HPLC measurements.

Time (min)	Mobile Phase Gradient		Flow Rate (mL·min ^{−1})
	Solvent A (%)	Solvent B (%)	
0	100	0	0.9
20	100	0	0.9
45	0	100	0.9
70	0	100	0.9
75	100	0	0.9

Solvent A: Methanol; Solvent B: 2-Propanol/Hexane = 4/5; Injection Volume: 1 µL; Column Temperature: 25 °C.

4. Conclusions

In summary, magnesium oxide catalysts supported on ZSM-5 zeolites and oxide supports were prepared by an impregnation method and all materials were tested in biodiesel production reaction in order to select the best catalytic system. The physicochemical properties of the catalysts were also correlated with the reactivity results in a biodiesel production process. The physicochemical properties were tested by BET, CO₂-TPD, FTIR and XRD techniques. The obtained activity results indicate that the reactivity of the synthesized catalytic systems in the transesterification reaction of rapeseed oil is influenced by the silicon to aluminum ratio for the support. Magnesium oxide catalyst supported on ZSM-5 zeolite with higher silicon to aluminum ratio gave higher triglyceride conversions and higher yields of FAME. The catalysts directly impregnated on the ammonium form of the NH₄-ZSM-5 zeolite exhibited higher TG conversion and yield to FAME in the transesterification reaction of rapeseed oil with methanol than the catalysts impregnated onto the hydrogen form of the HZSM-5 zeolite obtained by long-term heating. The most active catalyst system in the transesterification reaction was the 10% MgO/ZSM-5 (Si/Al = 280) catalyst, which showed the highest value of higher fatty acid methyl esters (94.6%) and the second-highest yield of triglyceride conversion (92.9%). Its high activity is explained by the high specific surface area, alkalinity and sorption properties in relation to methanol. The obtained activity results in the transesterification reaction clearly confirmed the potential application of MgO catalytic systems supported on zeolite as active materials for biodiesel production.

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