DOI: 10.1002/cssc.200900234 Hydrocracking of Ethyl Laurate on Bifunctional Micro-/Mesoporous Zeolite Catalysts

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Fossil raw materials such as crude oil, natural gas, and coal are still the most important resources for modern chemical industry. Nevertheless, efforts are made world-wide to substitute them for renewables. A sustainable source that supplies chemical products and fuels is biomass, the diversity of which extends from vegetable biomass over fats and oils to biogenic residues and wastes. From this perspective an important task for further developing biorefinery technologies is to transfer knowledge of catalytic and petrochemical processes in oil refining to the ecological conversion of renewable resources.

A promising strategy to cover the requirements for essential chemical products and fuels can be the use of vegetable oils. Their high energy content and good compatibility to the petrochemistry infrastructure makes them suitable substitutes for fossil resources.^[1,2] Based on these raw materials a wide chemistry is accessible. Recent investigations have demonstrated that oxygen-containing compounds as well as linear, branched, or aromatic hydrocarbons can be produced.^[1] Currently, the focus is on second-generation biofuels and light olefins such as ethene and propene, which are available by heterogeneously catalyzed conversions of vegetable oils. Controlling the product selectivity has proven to be problematic. However, there is a continued demand for research investigations towards the development of suitable, highly selective catalysts that produce specific and market-relevant chemical products and fuels based on vegetable oils.

Zeolites and zeolite-type materials with tailor-made structures and, by modifications, a wide range surface-chemical properties play an important role as catalyst components, due to their extremely large inner surfaces and adsorption capacities. Furthermore, the nature and concentration of active sites in the zeolite interior can be adapted to specific applications. Ordered mesoporous materials such as MCM-41 or SBA-15, with their larger pore sizes, may be used for heterogeneously catalyzed reactions of bulky reactants such as vegetable oils.

The pyrolysis of vegetable oil is a potential method for producing light olefins. Bakhshi et al. reported the total conversion of canola oil by thermal cracking in the range of 300– 500 °C with weight hourly space velocities (WHSVs) between 3.3 and 15.4 h^{-1} .^[3] Up to 37.1 wt% of light olefins and 13.6 wt% of aromatic compounds could be maintained as main products. Similarly, biomass can be converted into petroleum in a petrochemical refinery by catalytic cracking, hydro-

 [a] O. Busse, Dr. K. Räuchle, Prof. W. Reschetilowski Institute for Industrial Chemistry Department of Mathematics and Natural Sciences Dresden University of Technology Zellescher Weg 19, 01062 Dresden (Germany) Fax: (+ 49) 351-463 32658 E-mail: wladimir.reschetilowski@chemie.tu-dresden.de treating, and hydrocracking reactions.^[1] By using these conditions defined refinery products such as liquid petroleum gas, olefins, gasoline, diesel, and kerosene are available.

McCall et al. showed that in the presence of a heterogeneous catalyst the selectivity of light olefin formation can be enhanced.^[4] Vegetable oil was converted into ethene (8.7 wt%) and propene (22.4 wt%) by using H-ZSM-5 as catalyst. Throughout the catalytic cracking of vegetable oil on acid zeolite catalysts of the type H-ZSM-5, different reaction pathways lead to a broad range of products, including heavy hydrocarbons, oxygenates, paraffins (gasoline, diesel, kerosene), light olefins, light paraffins, aromatic compounds, crack gases, and coke.^[5] The cracking of rapeseed vegetable oil under fluid catalytic cracking (FCC) conditions was studied by Dupain et al.^[6] By using a commercial equilibrium FCC catalyst, gasoline- and diesel-range paraffins, aromatic compounds, and olefins were available. However, the amount of olefins was low owing to the high aromatization rate, up to 40 wt %. Bakhshi et al. investigated the production of C2-C4 olefins via the conversion of canola oil at atmospheric pressure in a fixed-bed reactor.^[7] In the presence of a potassium-modified H-ZSM-5 catalyst a maximum yield of 25.8 wt% was obtained at 500 $^\circ\text{C}$ and a WHSV of $1.8 h^{-1}$.

Ordered mesoporous materials can be used to improve the access to the inner surface. The conversion of fatty acids over mesoporous or composite micro- and mesoporous catalysts was demonstrated by Ooi et al.^[8,9] The conversion as well as the selectivity to lower olefins was enhanced by using the composite materials, in comparison to the pure micro- or mesoporous materials. Using MCM-41- or SBA-15-coated ZSM-5 resulted in a maximum of the light olefin fraction yield during the conversion of a fatty acid mixture. ZSM-5 coated with 30 wt% pure-siliceous SBA-15 enhanced the yield of propene to up to 33.5 wt%. This indicates that composite systems of both micro- and mesoporous materials, which combine the accessibility of the pores with a high surface acidity, improve the selective conversion of vegetable oils towards light olefins.

The reaction mechanism of hydrotreating vegetable oil on CoMo- and NiMo-catalysts reveals that the hydrogenation of unsaturated fatty acid residues leads to the formation of dicly-cerides, monoglycerides, acids, and waxes,^[10] which can be converted into heavy paraffins, propane, CO, and CO₂. The hydrocarbons can subsequently be isomerized to iso-paraffins or cracked to light olefins or paraffins.

The synthesis, characterization, and catalytic behavior of micro- and mesoporous composite materials have been reported by several authors (Van Bekkum et al.,^[11] Klemt et al.,^[12] Karrlson et al.,^[13] Mintova et al.,^[14] and Pinnavaia et al.^[15]). The improved transport of reactants to the active sites via larger mesopores (MCM-41) and a high acid-catalytic activity as well

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as apparent shape selectivity (ZSM-5) are the most important benefits of these composite materials.

The aim of the present work is to investigate the hydrocracking reaction of ethyl laurate (dodecanoic acid ethyl ester, Scheme 1) by using different bifunctional micro- and mesopo-



Scheme 1. Hydrocracking of ethyl laurate.

rous catalyst systems. This model compound was used because of its lower viscosity and melting point, in comparison to vegetable oils. The development of the catalyst is based on innovative supports. The micro- and mesoporous bifunctional catalyst samples used in this study are an acidic Al-MCM-41/ ZSM-5 composite as well as Al-MCM-41 and H-ZSM-5, loaded with nickel (1.73 wt%) and molybdenum (6.67 wt%). The surface acidity of the calcinated samples is characterized by temperature-programmed desorption of ammonia (TPAD; Table 1). By using these catalyst systems structure–effect relationships in the hydrocracking of ethyl laurate are investigated.

Table 1. Acidic properties of the investigated catalyst systems.						
Catalyst sample ^[a,b]	Si/Al ^[c]	Acidity ^[d]	Lewis/			
	(molar ratio)	[mmol(NH ₃) g ⁻¹]	Brønsted ^[d]			
NiMo/ZSM-5	26.7	1.14	1:2.41			
NiMo/(Al-MCM-41/ZSM-5)	25.8	0.64	1:1.95			
NiMo/Al-MCM-41	30.9	1.04	2.54:1			

[a] As calcinated. [b] Ni 1.73 wt%, Mo 6.67 wt%. [c] Bulk catalyst, by atomic absorption spectrometry (AAS). [d] By TPAD, with FT-IR (Brønsted 1450 cm⁻¹, Lewis 1620 cm⁻¹).^[18]

NiMo/Al-MCM-41, NiMo/ZSM-5, and NiMo/(Al-MCM-41/ZSM-5) were synthesized according to a procedure reported previously.^[16,17] The conversion of ethyl laurate was performed in a fixed-bed reactor under integral conditions. The influence of catalyst modifications on the product distribution was studied in dependence on the reaction temperature (300–500 °C) and process pressure (0–20 bar, hydrogen) at a constant space velocity WHSV = 10 h⁻¹.

As a result ethyl laurate was hydrocracked to a product mixture that consisted of organic liquid products, gaseous prod-

ucts, water, and coke. The main products were identified as light olefins (C_2-C_4) and aromatic compounds as well as *n*- and iso-paraffins in the gasoline and diesel range. During time-onstream all catalyst samples showed only slight deactivation, and conversion rates and product selectivities remained nearly



Figure 1. Influence of support material and temperature on the conversion of hydrocracking of ethyl laurate (WHSV = $10 h^{-1}$).

■ 400 °C, 5 bar ■ 500 °C, 5 bar

its weaker acidity (Table 1). However, at higher temperatures (500 °C) the conversion increased strongly. This can be explained by a higher Brønsted acidity of the NiMo/(Al-MCM-41/ZSM-5) sample compared to NiMo/Al-MCM-41. Increasing the temperature led to an increase of catalyst activity due to an intensification of the proton mobility. Further investigations showed that NiMo/ZSM-5 reached high conversion rates, even at lower temperatures of 400 °C.

It can be assumed that the acidity of the catalyst systems should also be reflected in the product distribution. Indeed, the nature of acid sites strongly influences the cracking mechanism and product distribution. Catalysts with high amounts of Brønsted acid sites such as NiMo/(Al-MCM-41/ZSM-5) and NiMo/ZSM-5 led to an improved selectivity towards C₃ and C₄ hydrocarbons (Table 2). However, a Lewis-acid-rich sample such NiMo/Al-MCM-41 is more selective to methane formation. The selectivity to light olefins was increased when using NiMo/(Al-MCM-41/ZSM-5), due to metal–support interactions that partly inhibit hydrogen transfer reactions (Table 3).^[19] The strength of the metal–support interactions can be derived from the location of peak maxima in temperature-programmed reduction (TPR) with hydrogen.

Especially the formation of the light olefins propene, 1butene, and ethene was enhanced in the presence of the

Table 2. Influence of the catalyst acidity on the yield of selected hydrocarbons at 500 $^\circ$ C and 5 bar.							
Catalyst	C ₁	C ₂	C ₃	C ₄	C₅	$\Sigma C_6 - C_{10}$	C ₁₁
	[wt%]	[wt %]	[wt %]	[wt%]	[wt%]	[wt%]	[wt %]
NiMo/ZSM-5	7.3	22.2	29.0	13.3	3.1	< 1.0	0.1
NiMo/Al-MCM-41	30.6	11.0	4.0	4.8	5.4	< 1.0	9.1
NiMo/(Al-MCM-41/ZSM-5)	3.9	17.9	24.6	22.1	8.6	< 1.0	1.8

constant in time. The conversion of ethyl laurate increased with increasing reaction temperature and hydrogen pressure. In comparison to other support materials NiMo/(Al-MCM-41/ ZSM-5) showed a lower conversion at 400°C (Figure 1) due to

Table 3. Influence of the cata	alyst acidity or	the yield of lig	ht olefins at 500	°C, 5 bar, and a W	HSV of 10 h^{-1} .			
Catalyst	Ethene [wt %]	Propene [wt %]	1-Butene [wt %]	iso-Butene [wt %]	<i>trans</i> -2-Butene [wt %]	<i>cis</i> -2-Butene [wt %]	Σ	τ _{max} ^[a] [°C]
NiMo/ZSM-5	-	-	7.3	0.3	_	-	7.6	425
NiMo/Al-MCM-41	1.0	2.4	-	2.0	1.2	0.9	7.5	425
NiMo/(Al-MCM-41/ZSM-5)	10.5	27.2	1.0	12.9	5.2	3.7	60.5	525
[a] TPR with 10% H_2 in Ar, 10	°Cmin ⁻¹ temp	erature rate.						

NiMo/(Al-MCM-41/ZSM-5) mixed system, compared to NiMo/ Al-MCM-41 and NiMo/ZSM-5 (Table 3). For this composite material a maximum yield of 60 wt % light olefins (C_2-C_4) was obtained.

This work demonstrates that bifunctional micro-/mesoporous zeolite systems can be successfully used for hydrocracking of ethyl laurate as a model compound for vegetable oils. The catalytic activity and selectivity of the investigated catalyst samples depends strongly on their surface acidity. Brønsted acid sites mainly catalyze the formation of C_3 and C_4 hydrocarbons. On the other hand, Lewis acid sites dominate the formation of methane. Catalyst systems with strong metal–support interactions induce an increase in the yield of olefins owing to inhibition of hydrogen transfer reactions^[19].

Experimental Section

The synthesis of support materials has been reported earlier.^[16,17] The obtained supports were loaded with nickel (1.73 wt%) and molybdenum (6.67 wt%) by a wet-impregnation method. The resulting catalyst samples were analyzed by physico-chemical characterization methods (XRD/SAXS, AAS, nitrogen sorption, TPAD, and TPR). The surface acidity and strength and nature of the acid sites of the catalyst samples were characterized by temperature-programmed desorption of ammonia, followed by FT-IR spectroscopy. The Lewis/Brønsted ratio was determined by integrating the intensities of specific bonds (Brønsted 1450 cm⁻¹, Lewis 1620 cm⁻¹).

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Keywords: biomass · heterogeneous catalysis · olefination · porous materials · zeolites

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