CATALYTIC ACTIVITY OF SMECTITES ON DIMERIZATION OF OLEIC ACID

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A series of dimerization experiments were conducted to investigate the relationship between dimerization yield and crystallochemical composition of five smectite minerals used as catalysts. Effect of interlayer cations and acid treatment of one montmorillonite was also investigated. The maximum dimer yield was obtained with magnesium as interlayered cation. Aluminium and calcium varieties yielded lower amounts of dimers. Addition of sodium carbonate (natrification) was detrimental to dimer production. Dimer recovery was increased by the use of montmorillonite partialy decomposed by hydrochloric acid. Variations in the crystallochemical composition of smectites had little effect on the amount of dimer produced. High iron content in the catalyst lowered the quality of the dimerization products.

Smectites are clay minerals composed of negatively charged 2 : 1 layers separated by hydrated interlayer cations. One octahedral sheet is layered between two tetrahedral sheets. In dioctahedral smectites, such as montmorillonites, beidellites or nontronites, heterovalent substitution of Al(III) for Si(IV) in tetrahedra and/or Mg(II) or Fe(II) for Al(III) in octahedra confers a net negative charge on the sheets. The negative charge is balanced by exchangeable cations in the interlayer space. Smectite minerals are known for their ability to swell, high surface area and high cation exchange capacity.

Smectite are frequently employed as catalysts in various reactions[1 – 4]. Typically, the clays act as a solid source of protons[1]. The protons responsible for the acid character of the smectite catalyst are produced by polarization of interlayer water[5]. The ability of smectite minerals to contribute protons for catalytic purposes is enhanced by treating them with an acid to form H-smectites. These are a good source of protons, but they are also known as unstable materials undergoing autotransformation to (H,Al,Mg)-forms[6]. Acid treatment of montmorillonite was reported recently to increase significantly its effectiveness as a support for $ZnCl_2$ Friedel–Crafts alkylation catalysts[7] and as a catalyst for the dehydration and esterfication of 1-hexanol[8]. Acid treatment of bentonites is widely used in industry for bleaching earth and catalyst production.

A yield limit of about 60 wt.% of dimers and trimers was reported for the dimerization of oleic acid with a montmorillonite catalyst[9]. A hydrogen transfer reaction was found to be involved and a reaction model was proposed[9 – 11]. Negative layer charge of montmorillonite catalyst affected significantly the dimerization of unsaturated fatty acids[12].

The two objects of this work were (i) to investigate the relation between the crystallochemical composition and catalytic activity of smectites separated from some Czech and Slovak bentonites to the dimerization of oleic acid, and (ii) to improve the activity of some of these catalysts.

EXPERIMENTAL

Materials

Under 2-μm fractions of five Czech and Slovak bentonites were separated, Ca^{2+} saturated, washed free of excess ions, dried at 60 °C and ground to pass a 0.2 mm sieve. Their chemical composition is given in Table I. Minerals present in the sample were identified by X-ray diffraction and infrared spectroscopy (Table II)[13]. Significant amount of iron bound in goethite was found in three samples (52% of total Fe in R, 67% in S and 70% in ČV) by low temperature Mössbauer assay[14]. Structural formulas of smectites, the main minerals present in the clay used, calculated from the acid dissolution data[13] are given in Table III.

Various cationic forms were prepared from the Ca-saturated Jelšový potok sample. Samples were washed three times with 10 wt.% $MgCl_2$ or $AlCl_3$ solution to form the Mg- and Al-forms, respectively. After that the excess ions were washed out with water. The preparated Mg-form was divided into two parts which were dried to constant weight at 60 and 250 °C, respectively, to obtain materials with different water content and different acidity of protons in the coordination sphere of interlayer Mg. Sodium carbo-

TABLE I

Chemical composition of the catalysts used

Species	Sample, wt.%[a]				
	JP	H	S	R	ČV
H_2O (105 °C)	6.75	8.96	7.96	10.14	10.60
SiO_2	60.01	50.08	49.01	49.83	44.58
Al_2O_3	20.77	14.42	17.17	13.10	18.64
Fe_2O_3	3.75	7.71	15.47	17.51	18.35
FeO	–	4.91	0.47	0.05	0.04
CaO	2.55	4.14	1.81	3.15	1.17
MgO	4.11	2.92	2.68	2.70	2.47
TiO_2	0.24	5.08	3.38	5.09	3.50
K_2O	0.17	0.71	0.75	0.72	0.07
Na_2O	0.11	0.06	0.13	0.20	0.05
H_2O (1 000 °C)	7.64	9.17	8.58	7.04	10.21
Σ	99.35	99.20	99.30	99.39	99.08

[a] JP Jelšový potok, bentonite from central Slovakia; R Rokle, S Střimice, ČV Černý vrch, H Hroznětín, bentonites from northwest Bohemia.

nate was added at 5 weight percent level to the Ca-form and the mixture was ground in percussive grinder to obtain the Ca/Na form. (H,Al)-forms with various degree of clay decomposition were prepared by reacting the Ca-form with 6 mol dm^{-3} HCl at 95 °C (duration 10 min, 1.5, 3, and 6 h). The amount of dissolved Al was determined by aluminon method[15]. All catalysts were dried to constant weight at 60 °C (except JP Mg(250), were the indicated temperature was used) and ground to pass a 0.2 mm sieve.

Methods

Dimerization experiments were carried out in nitrogen atmosphere in a 1600 ml autoclave with an electronically operated pulse stroke stirrer (72 pulses/min). An amount of 500 g technical grade oleic acid (main fatty acid components: 12 : 0 1.1%, 14 : 0 2.1%, 16 : 0 4.6%, 16 : 1 5.8%, 18 : 0 1.4%, 18 : 1 61.2%, 18 : 2 13.5%, higher than 20 : 0 7.9%, others less than 1%), 40 g catalyst and 25 g water were used. In

TABLE II
Minerals identified in the catalysts used

Mineral[a]	Catalyst[b]				
	JP	R	S	ČV	H
Montmorillonite	X	–	X	X	X
Fe-beidellite	–	X	–	–	–
Kaolinite	–	–	m	m	m
Anatase	–	m	m	m	m
Goethite	–	G	G	G	–

[a] Refs[13,14]. X Major component, m minor component, G more than 50% of total iron bound in goethite. [b] For designation see Table I.

TABLE III
Structural formulas of smectites calculated from acid dissolution data[a] per $O_{20}(OH)_4$

Sample	Interlayer	Tetrahedra		Octahedra		
	M^+	Si	Al	Al	Fe	Mg
JP	0.74	7.69	0.31	3.29	0.27	0.44
H	1.62	7.50	0.50	2.32	1.41[b]	0.27
S	0.84	7.74	0.26	2.99	0.52[c]	0.49
R	1.50	6.87	1.13	2.01	1.64	0.35
ČV	0.50	7.95	0.05	3.19	0.37	0.44

[a] For method see ref.[13], designation see Table I; [b] Fe(II) 0.85, Fe(III) 0.56; [c] Fe(II) 0.09, Fe(III) 0.43.

experiments with various forms of the sample JP only 20 g catalyst were employed. The reaction mixture was heated up to 245 °C in about 60 min. The same heating rate was used in all experiments. The mixture was kept at this temperature and pressure of 1.2 MPa for 4 h. The reaction was stopped by releasing the pressure. The suspension was cooled to 120 °C and filtered without contact with air. All reactions were run in duplicates. A gas chromatographic method[16] was used for analysis of products.

RESULTS AND DISCUSSION

The analyses of the mixtures of reactions products after dimerization with various smectites are given in Table IV. No relationship was found between the amount of monomers, dimers and/or higher oligomers, and tetrahedral, octahedral or total layer charge of the catalyst. Thus, the composition of the clay layers has an insignificant effect on the dimerization yield. This is in contradiction with ref.[12], where significant effect of total layer charge was reported. The amount of monomer in the reaction mixture was in three cases close to the expected 40% (ref.[9]), while it was higher with ČV and S (Table IV).

The products obtained from the reactions with H, S, R and ČV samples were darker than the product obtained with the JP catalyst. The darker product may be a consequence of high iron content in the Bohemian bentonites. Significant amount of this iron is bound in goethite (in S, ČV and R) or is ferrous (in H)[14]. However, additional assay is needed to identify the darker compounds.

The highest yield and the lightest products were attained with the JP bentonite. This clay was chosen for the next set of experiments to investigate the effect of interlayer cations on the reaction. Only 4 wt.% catalyst were used in this set of reactions. The results are given in Table V. The highest dimer yield (42 wt.%) was obtained with the Mg(250) catalyst, while the Mg(60) was slightly less effective. The Al- and Ca-forms produced lower yields than the Mg-forms, and the Ca/Na catalyst was totally non-

TABLE IV
Layer charge (in electrons per structural unit) of smectites, and analyses of reaction products (8 wt.% catalyst used)

Catalyst[a]	Charge, e/$O_{20}(OH)_4$		Yield, wt.%		
	tetrahedra	octahedra	monomer	dimer	HP[b]
JP	0.31	0.44	38 ± 4	51 ± 2	11 ± 2
H	0.50	1.12	43 ± 4	52 ± 5	5 ± 1
S	0.26	0.58	58 ± 3	38 ± 1	4 ± 2
R	1.13	0.35	44 ± 4	46 ± 1	11 ± 3
ČV	0.05	0.44	49 ± 3	44 ± 2	7 ± 5

[a] For designation see Table I; [b] HP higher polymers.

effective. The effectiveness of the Mg-forms is a consequence of the higher acidity of protons in the solvatation sphere of Mg cation[17]. Dehydration at 250 °C decreases the amount of water molecules solvating Mg cations, and the acidity of the protons in the solvation sphere is increased. This showed up in the increased yield of the dimer. Low content of higher polymers was observed with all catalysts used (Table V).

Addition of Na_2CO_3 negatively affected the dimerization yield. The reaction of CO_3^{2-} anion with protons decreases their concentration and availability for catalyzed reaction. Neutralization of protons by carbonate anions was found to decrease the swelling of Na_2CO_3 treated H-montmorillonite Jelšový potok[18].

The effect of hydrated exchangeable protons in the interlayer space and montmorillonite structure decomposition on dimerization was tested using the JP samples treated in HCl. This treatment causes the rapid exchange of H for Ca in the interlayers, and the gradual decomposition of the mineral. The acidity of the clay depends on the level of structure decomposition. The highest dimerization yield was found with the catalyst after 1.5 h leaching in HCl, with 18% dissolved aluminium (Table V). This corresponds reasonably to the results of previous experiments with Askangel montmorillonite, where both highest surface acidity and highest catalytic activity were found after one hour leaching[17] in HCl.

TABLE V
Reaction products with 4 wt.% JP bentonite saturated with various interlayer cations

Interlayer cation	Yield, wt.%		
	monomer	dimer	HP[a]
Ca	63 ± 3	33 ± 2	4 ± 1
Ca/Na	93 ± 1	5 ± 2	2 ± 1
Mg (60)[b]	56 ± 3	38 ± 1	6 ± 2
Mg (250)[b]	53 ± 3	42 ± 1	5 ± 2
Al	64 ± 2	34 ± 3	2 ± 1
H, Al (0.04)[c]	61 ± 3	34 ± 4	5 ± 1
H, Al (0.18)[c]	50 ± 3	46 ± 5	4 ± 2
H, Al (0.28)[c]	56 ± 2	42 ± 1	3 ± 1
H, Al (0.49)[c]	62 ± 3	34 ± 2	3 ± 1

[a] HP higher polymers; [b] temperature of drying given in brackets; [c] the number in brackets shows the portion of octahedral Al dissolved in the course of HCl treatment.

CONCLUSIONS

Crystallochemical composition of smectites had little effect on their activity as catalysts in dimerization of oleic acid in our experiments. High ferrous or goethiteic iron content in the catalyst lowered the quality of the dimerization products. The catalytic activity can be improved by exchange of interlayer cations for Mg, or by partial decomposition of the clay in hydrochloric acid. Addition of Na_2CO_3 to montmorillonite strongly decreases the yield of dimerization.

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