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Mesoporous aluminosilicates- highly efficient catalysts of oligomerization of α-olefins

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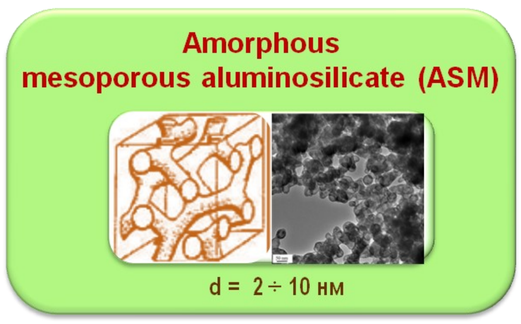
Introduction

The oligomerization products of α-olefins are widely used as high-octane components of fuels, lubricants, solvents, plasticizers, etc.

The production of oligomers includes the catalytic oligomerization and the hydrogenation of the products obtained. The drawbacks of Bronsted and Lewis acids, metalorganic catalysts, used in these processes, are well known and it stimulates the search for new, more efficient and environmentally friendly catalytic systems.

The aim of this work is to develop heterogeneous catalytic methods for oligomerization of light (C_5) and higher α-olefins (C_8-C_{16}) based on the use of mesoporous aluminosilicates ASM.

Experiment



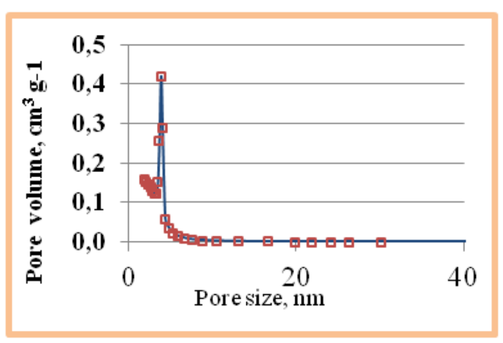


Fig 1. Pore size distribution of ASM

Indicators	ASM
Si / Al	40, 80, 160
S BET, m^2 g^{-1}	600-700
V mesopore, cm^3 g^{-1}	0,9-1,0
V micropore, cm^3 g^{-1}	0,05
C_{H+}, mmole g^{-1}	300- 600

Aluminosilicates ASM (Si/Al ratio = 40, 80 and 160) were prepared by sol-gel synthesis.

Catalytic transformations of α-olefins C_5-C_{16} were carried out in autoclave at temperature 60–250 ºC for 1–5 hours, the catalyst content was 10–30 % wt.

The catalysts were characterized by the methods of X-ray fluorescence spectrometry, low-temperature adsorption of nitrogen, SAXS, ^{27}Al MAS NMR spectroscopy, IR- spectroscopy in combination with the adsorption of the probe CO molecule, TEM.

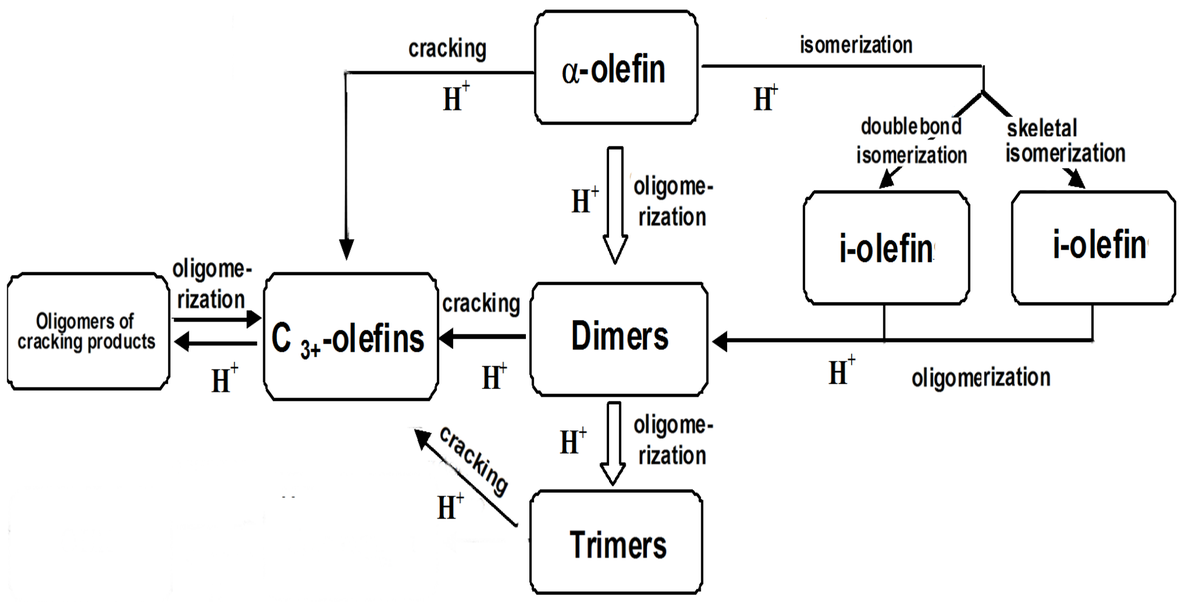
Identification of products of reactions was carried out by chromatography-mass spectrometry (GC-MS), ^{1}H and ^{13}C NMR, method DEPT NMR.

Results

It has been established that aluminosilicates exhibit high activity in the oligomerization of of C_5-C_{16} olefins. The maximum conversion of olefins was observed on a sample with a molar ratio of Si/Al=40, which has the highest acidity. The selectivity for pentene oligomers on an ASM-40 sample reaches 100%, and di-tri- and tetramers are present in the oligomers.

Oligomerization of octene and decene proceeds with the formation of predominantly dimers (37-50%) and trimers (32-39%). The selectivity for dodecene oligomers is 74%, and for hexadecene oligomers -66%. Dimers and trimers remain products of oligomerization, although the content of trimers decreases from 20% (C_{12}) to 9% (C_{16}).

Note that, unlike zeolites, we did not observe the formation of degradation products of the initial monomers and the obtained oligomers on mesoporous aluminosilicates. This indicates the absence or very low cracking activity of these catalysts.



Scheme 1. **Conversion of linear a-olefins in the presence of aluminosilicates ASM**

Mesoporous aluminosilicate ASM

C_5: conversion up to 100%; selectivity - dimers (40-70%), trimers (20-50%), tetramers (10-25%);
C_{8-10}: conversion up to 100%; selectivity - dimers (37-50%), trimers (30-40%);
C_{12}: conversion up to 100%; selectivity - dimers (80%), trimers (20%);
C_{16}: conversion up to 100%; selectivity - dimers (91%), trimers (9%).

Recent Publications

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3. Agliullin M, Danilova I, Faizullin A, Amarantov S, Bubennov S, Prosochkina T, Grigor'eva N, Paukshtis E, Kutepov B (2016) Microporous and Mesoporous Materials 230:118-127.
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Acknowledgments

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Conclusions

It was shown high effectivity mesoporous aluminosilicates ASM in the synthesis of oligomers of olefins C_5– C_{16}. The most active in the reaction of samples with a high concentration of acid sites (molar ratio of Si/Al=40). Under the conditions studied, complete conversion of olefins was achieved. The selectivity of the formation of oligomers decreases with lengthening of the carbon chain of the olefin. Pentene, octene and decene oligomers were synthesized on mesoporous aluminosilicates with a yield of 100%. The degree of oligomerization of the obtained products is 2-5. C_{12}– C_{16} olefins were predominantly converted into dimers over mesoporous aluminosilicate with selectivity up to 70%. Unlike zeolites, aluminosilicates have a very low cracking ability of oligomers.

Biography

Nellya G. Grigor'eva – Doctor of Science, Leader Researcher, Catalysts Preparation Laboratory, Institute of Petrochemistry and Catalysis, Russian Academy of Sciences.

Under her leadership, new heterogeneous-catalytic methods for the production of components for gasolines, diesel and jet fuels, synthetic lubricants by oligomerization of C5-C-16 linear olefins, cyclenes and vinylarenes, Selective methods for producing oxygen-containing derivatives of norbornene and styrene, methods for the synthesis of α, β-unsaturated aromatic ketones, basic N-heterocyclic compounds in the presence of crystalline and amorphous alumosilicates have been developed.

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