

Biodiesel improvement by skeletal isomerization on hierarchical zeolites

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Significance and Relevance

Biodiesel worldwide production is still rising and will do so for many years, as the delays of electrification of the fuel production for heavy-duty transport justify an intermediate introduction of bio-based renewables. Shift to continuous-flow processes and improvement of the properties of enoic esters from vegetable or recycled oils require new custom-tailored heterogeneous catalysts.¹

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, Renewable resources conversion Preferred presentation: Poster

Introduction and Motivations

The recrystallization of zeolites in cetyltrimethylammonium (CTA) solution is an accepted method to open a hierarchical micro-mesoporous network and improve the accessibility of the active sites.² Micro-mesoporous hierarchical zeolites can provide significant improvements in selectivity and stability of the methyl oleate isomerization in flow reactors, overcoming previously observed site passivation.³

Materials and Methods

Parent ferrierite (FER-PAR, Si/Al 9.7, BET surface area 394 m²g⁻¹, α S external surface area 15 m²g⁻¹) and dealuminated faujasite (Y30-PAR, Si/Al 30, BET 716 m²g⁻¹, α S 110 m²g⁻¹) were proton exchanged, recrystallized in cetyltrimethylammonium (CTA) solution, and calcined at 550°C, obtaining recrystallized FER-REC (Si/Al 6.6, BET 427 m²g⁻¹, α S 159 m²g⁻¹) and Y30-REC (Si/Al 24, BET 837 m²g⁻¹, α S 583 m²g⁻¹) catalysts that were tested for methyl oleate isomerization in batch autoclave (solventless, 285°C, 6 h) or in continuous flow reactor (285°C, N₂ flow, WHSV 3.5 h⁻¹).

Results and Discussion

The CTA recrystallization treatment has been applied to two kinds of zeolites with different microporosity - 10-member ring (10MR) medium size-micropore ferrierite and 12MR large-micropore high-silica faujasite - producing different structural mesoporosity in the two kinds of zeolites, with formation of MCM-41-like wormlike mesopores in faujasite and opening of a constrained negative-crystal mesoporosity in ferrierite (see Fig. 1A).^{4,5}

Results of methyl oleate skeletal isomerization at 285 °C over faujasite and ferrierite catalysts are reported in Fig. 1B and 1C, respectively. In batch experiments (color bars in the figures), the yield of branched isomers on the parent zeolites was 27% on Y30-PAR and 55 % on FER-PAR. The difference between the two kinds of zeolites depends more on the shape selectivity of ferrierite for alkene isomerization than on the different amount of Brønsted acid sites. CTA recrystallization induces a limited yield improvement of 2% for Y30-REC and 4 % for FER-REC. In the case of the flow reactor experiments (lines with dots in Fig.1B and 1C), the yield of branched products on the parent zeolites is always lower than in the batch experiments and rapidly decreases with time-on-flow, until 4% on Y30-PAR and 8 % on FER-REC after 7 h. When the recrystallized catalysts are used, the distribution of products on the two zeolites is completely different. In the case of faujasite Y30-REC (Fig. 1B, line b), the recrystallization induces a moderate improvement of yield and does not prevent a severe deactivation, reaching 9 % at 8 h time-on-flow. In the case of FER-REC (Fig.1C, line d), the yield of



branched monoenoic methyl esters rapidly rises to 53% and remains stable around this value for 8 h time-on-flow, at 98 % oleate conversion.

It has been surmised that the better results obtained on recrystallized ferrierite catalysts are due both to the well-known shape selectivity of the ferrierite structure for alkene isomerization reactions and to the solvent effect of condensed liquid phase in the constrained mesoporosity. It is likely that the condensate in the constrained porosity of FER-REC exert a washing effect on the poisoning deposits on the active sites, in a similar way of the effect of the pressurized liquid phase in the batch reactor experiments.



Figure 1 N₂ sorption isotherms for recrystallized samples (A) and branched isomer yield on faujasite (B) and ferrierite (C) catalysts (bars are batch results whereas lines and dots are continuous flow results vs. time-on-flow) Y30-PAR (a), Y30-REC (b), FER-PAR (c) and FER-REC (d).

Moreover, the higher continuous-flow methyl oleate isomerization on ferrierite induced a significant improvement of the cold-flow properties of the products, with freezing points on average 8 °C lower than for faujasite catalysts.

It appears that the limitations of catalyst stability in continuous flow process can be overcome by coupling the well-known shape selectivity of ferrierite for olefin isomerization with a mesopore shape able to provide an adsorbed liquid-mimicking phase. A correct choice of both micropore and mesopore architecture of hierarchical zeolites provides significant improvements in selectivity and stability of the methyl oleate isomerization in flow reactors.³

References

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