Transesterification of Rapeseed Oil in the Presence of Basic Zeolites and Related Solid Catalysts

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ABSTRACT: The transesterification of rapeseed oil with methanol was performed by reflux of methanol over cesium-exchanged NaX faujasites, mixed magnesium-aluminum oxides, magnesium oxide, and barium hydroxide for different methanol-to-oil ratios. Over cesium-exchanged NaX faujasites and mixed magnesium-aluminum oxides, a long reaction time and a high methanol-to-oil ratio are required to achieve both high oil conversion and high yields in methyl esters. However, over a 300 m^2/g magnesium oxide, methanol-to-oil ratios and reaction times are significantly reduced to obtain both high oil conversion and high yield in the methyl esters, particularly when the hydroxide precursor is calcined at 823 K. Finally, preliminary results with other basic solids such as barium hydroxide have shown a very high activity and a very high yield in esters. This catalyst is particularly effective since, for a methanol-to-oil ratio of 6, at reflux of methanol and after a reaction time of only 1 h, the oil conversion is about 80% with a nearly quantitative ester molar fraction.

Paper no. J9957 in *JAOCS 78,* 1161–1165 (November 2001).

KEY WORDS: Rapeseed oil, solid basic catalysts, transesterification, triglycerides.

Transesterification of vegetable oils with methanol (Scheme 1) is a permanent challenge to produce fatty acid methyl esters which can then be used as (i) raw materials for the chemical industry for the production of isopropyl esters and fatty alcohols, (ii) as biodiesel, and (iii) as precursors of nonionic biodegradable surfactants such as alkanolamides and alkyl glucosides (1).

Although the reaction proceeds nicely, even on an industrial scale, in the presence of sodium methylate or sodium or potassium hydroxide as catalysts, homogeneous catalysts are expected to be replaced in the near future by heterogeneous catalysts mainly because of environmental constraints and simplifications in the existing processes.

Among the different heterogeneously catalyzed processes, some interesting results were obtained at reflux of methanol, with a methanol-to-oil ratio of 6 and after 12 h of reaction in the presence of bulk or supported basic oxides, in particular CaO/MgO oxides (2). However, it was somewhat surprising to find MgO as an inactive catalyst (2,3) as well as natural clays or zeolites (3).

Guanidines grafted on cellulose, polystyrene/divinylbenzene resins, and polyurethanes were found to be less active than their homogeneous analogs. The loss of activity was attributed to the leaching of the anchored base from the polymer. In a similar manner, encapsulated guanidines in the supercages of a hydrophobic Y-zeolite led to a low activity, probably owing to the slow diffusion of triglycerides through the channels of the Y-zeolite and steric hindrance (1).

More recently, Corma *et al.* (4) showed that basic solid catalysts such as Cs-MCM-41, Cs-sepiolite, magnesium oxide, and hydrotalcites were efficient catalysts for the transesterification reaction between triglycerides and glycerol, in particular with MgO as catalyst. The results obtained were "as good as those obtained using the less attractive and more costly processes reported in the patent literature and in agreement with the European Union quality requirements."

In the present work, we report the results we have obtained in the transesterification of rapeseed oil in the presence of a series of catalytic systems known for their relatively strong basic properties (5) as well as for their reuse facility, namely, Cs-exchanged NaX faujasites, a commercial hydrotalcite, magnesium oxide, and barium hydroxide.

EXPERIMENTAL PROCEDURES

Reactants. Rapeseed oil (food-grade, acid-free, C_{18} over 97%) and methanol (99.8% purity) were used without further purification.

Catalysts. Cesium-exchanged NaCsX zeolites were prepared from the sodium form NaX (Aldrich, St.-Quentin Fallavier, France) by exchange with cesium chloride according to standard procedures already reported in the literature (6). The exchange ratios were obtained from elemental analyses. The different cesium-exchanged NaCsX zeolites were calcined in air flowing at 673 K prior to use. The specific surface areas are close to 450 m^2/g.

Hydrotalcite used in this work was KW 2200 from Kyowa (Paris, France) with an aluminum molar fraction of 0.3. It was calcined at 723 K prior to use. The specific surface area measured is 160 m^2/g.

Magnesium oxide was prepared from the brucite-like magnesium hydroxide from Strem Chemical (Bischheim, France). It was calcined at 723 or 823 K. From BET measurements, the surface area was calculated as 300 m^2/g for the oxide calcined at 723 K. At 823 K, a slight decrease of the specific surface area should have been observed.

Barium hydroxide was used after activation at 473 K, as proposed in the literature for the most active form (7).

Part of this work was presented at the 91st AOCS Annual Meeting, San Diego, California, April 2000.

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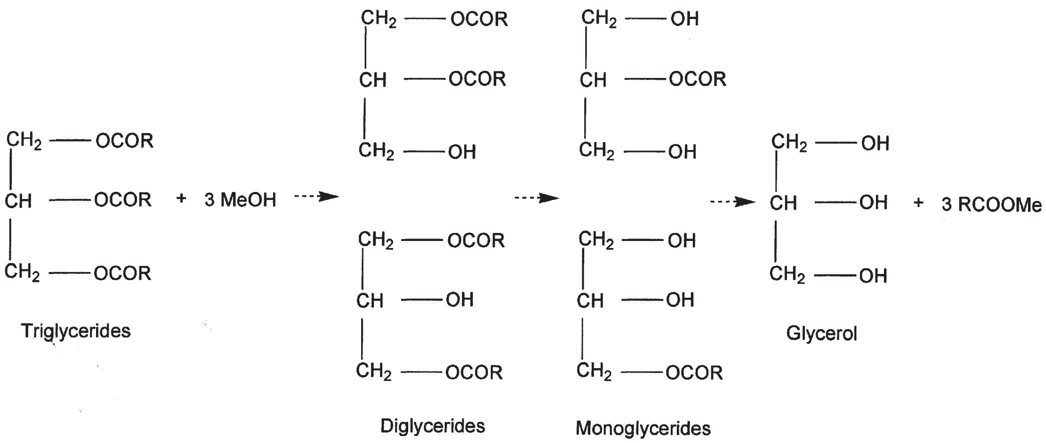

SCHEME 1

Procedure. Except where otherwise mentioned, the general procedure was typically as follows: the freshly calcined catalyst (0.5 g) was rapidly added to 63 mL of anhydrous methanol in a magnetically stirred (700 rpm) 100-mL glass reactor operating in a batch mode. At the reflux of methanol, 5 g of rapeseed oil was added dropwise at a rate such that the reflux was maintained. The methanol-to-oil molar ratio varied from 6 to 275 moles of methanol for 1 mole of oil, and the reaction time varied from 1 to 22 h.

Analyses. Analyses were performed by high-performance liquid chromatography (HPLC) using a Shimadzu (Paris, France) LC-6A pump and a refractive index RID-6A detector, and controlled by a PC with a software package (ICS). A Merck RP18 (C18) column (Darmstadt, Germany) was used, and the mobile phase was methanol/isopropanol (60:40, vol/vol) at 0.4 mL/min for the detection of esters and 1.0 mL/min for the detection of triglycerides. *N*-Octadecane was used as an external standard. The fatty acid methyl ester molar fraction (%) is given as methyl ester concentration/Σ (methyl ester + mono- + di- + triglycerides) × 100. The selectivity in methyl ester (%) is given as methyl ester concentration/Σ (methyl ester + mono- + diglycerides) × 100. The conversion is defined as the concentration ratio of transformed oil to initial oil × 100. The mass balance is defined as the concentration ratio of identified products to oil transformed × 100.

RESULTS AND DISCUSSION

Catalyst screening. Initial screening experiments were conducted in order to identify the most promising solid catalysts for the transesterification of rapeseed oil, taking into account the results already reported in the literature and the operating conditions as close as possible to those used for the homogeneous reaction, as well as the facility of regeneration of the solid catalyst for a further reuse. Cesium-exchanged X-zeolites, hydrotalcites, magnesium oxide, and barium hydroxide were then chosen since it has already been shown that they were not subject to lixiviation phenomena, with respect to what occurred with bulk or alumina-supported potassium carbonate.

NaCsX zeolites: Influence of the exchange ratio of cesium. Under the following operating conditions: 0.5 g of catalyst, 63 mL of methanol, 5 g of rapeseed oil, methanol-to-oil molar ratio of 275, 22 h of reaction time at methanol reflux, the experimental results concerning the influence of the cesium exchange rate on ester molar fraction, mass balance, oil conversion, and ester selectivity for the transesterification of rapeseed oil with methanol in the presence of Cs-exchanged NaX are reported in Table 1. Under those operating conditions, in particular for a high methanol-to-oil molar ratio, a maximum in the activity is observed at around 30% cesium content. As the level of cesium exchange increases, steric constraints would play a role and would lead to a decrease in activity. Formation of aggregates at the entrance of the crystal would lower the migration of the reactants to the catalytic sites (8).

Influence of the catalyst weight. Under the following operating conditions: catalyst weight from 0.25 to 2 g, 63 mL of methanol, 5 g of rapeseed oil, methanol-to-oil molar ratio of 275, 22 h of reaction time at methanol reflux, the experimental results concerning the influence of the catalyst weight on ester molar fraction, mass balance, oil conversion, and ester selectivity for the transesterification of rapeseed oil with methanol in the presence of Cs-exchanged NaX are reported in Table 2. The ester molar fraction increases proportionally with the catalyst weight and then reaches a plateau representative of near completion of the reaction. A nearly quantitative yield in ester is obtained after 22 h of reaction for about 2 g of catalyst.

Influence of the methanol-to-oil molar ratio. Under the following operating conditions: 0.5 g of catalyst, 5 g of rapeseed oil, methanol-to-oil molar ratios between 15 and 275, and 22 h of reaction time at methanol reflux, the experimental results concerning the influence of the methanol-to-oil molar ratio on ester molar fraction, mass balance, oil conversion, and ester selectivity for the transesterification of rapeseed oil with methanol in the presence of the NaCs(34)X zeolite are reported in Table 3. From the results obtained, it is shown that the reaction cannot operate with a too low methanol-to-oil ratio in the presence of the NaCs(34)X zeolite. This phenomenon is not due to the weaker solubilization of the oil in

TABLE 1
Influence of the Cesium Exchange Ratio for NaCsX Catalysts[a]

Catalyst	Cs exchange rate (%)	Conversion (%)	Selectivity (%)	Ester molar fraction (%)	Mass balance (%)
NaCs(0)X	0	9	88	24	91
NaCs(34)X	34	70	96	88	96
NaCs(43)X	43	55	94	82	90
NaCs(54)X	54	20	91	49	83

[a] 0.5 g of catalyst, 63 mL of methanol, 5 g of rapeseed oil, methanol-to-oil molar ratio of 275, 22 h of reaction time at methanol reflux.

TABLE 2
Influence of the Catalyst Weight for NaCsX Catalysts[a]

Catalyst weight (g)	Catalyst	Conversion (%)	Selectivity (%)	Easter molar fraction (%)	Mass balance (%)
0.25	NaCs(34)X	34	90	61	89
0.5	NaCs(34)X	70	96	88	96
0.5	NaCs(43)X	55	94	82	90
1.0	NaCs(43)X	76	93	91	92
2.0	NaCs(34)X	—	—	99	—

[a] 63 mL of methanol, 5 g of rapeseed oil, methanol-to-oil molar ratio of 275, 22 h of reaction time at methanol reflux.

methanol. By contrast, glycerol could act as a poison since, once formed, it precipitates relatively rapidly, whereas it is soluble for methanol/oil ratios over 30.

Catalyst recycling. It has also been shown that the catalyst could be easily recycled after filtration and calcination at 673 K with a 25% loss in the ester yield (66% instead of 88%) in the presence of the NaCs(34)X catalyst. This loss does not result from a leaching phenomenon since the cesium content was found to be the same after reaction, but could result from the presence of glycerol or triglycerides which were not removed by calcination.

Conclusion. In order to conclude this part concerning the series of cesium-exchanged NaX catalysts, the experimental results obtained are then relatively far from the results and operating conditions used industrially with homogeneous catalysts (9).

Hydrotalcites. Layered double hydroxides or hydrotalcite-like compounds with different Al/(Al + Mg) atomic ratios have been shown to be efficient catalysts in the glycerolysis of rapeseed oil with a maximum in activity for a Al/(Al + Mg) atomic ratio of 0.2 (4).

In the present work, methanolysis of rapeseed oil was carried out in the presence of the KW 2200 commercial hydrotalcite with an aluminum molar fraction of 0.3 under operating conditions similar to those reported for the Cs-exchanged NaX zeolites. Experimental results are reported in Table 4.

In the absence of calcination, the KW 2200 catalyst is not particularly active, 12.5% of conversion after 22 h of reaction time (Table 4, entry 1). After calcination at 723 K, the catalyst is then in the form of a mixed magnesium aluminum oxide, the corresponding oil conversion is 34% (Table 4, entry 2) for the same reaction time, but lower than for the NaCs(34)X zeolite (Table 4, entry 3). Even after rehydration leading to an increase in the basic properties (hydroxide ions are then intercalated in the lattice), no improvement of the catalytic activity was observed.

In fact, as mentioned by Corma *et al.* (4), the presence of strongly basic catalytic sites resulting from the addition of Al_2O_3 into MgO does not improve the catalytic performances compared to MgO alone, which is active enough for carrying the transesterification reaction.

Magnesium oxide: Influence of the temperature of calcination. Whether the calcination of magnesium hydroxide is carried out in the presence of air or nitrogen flow has no significant consequence on oil conversion, ester molar fraction and ester selectivity, whatever the temperature of calcination (Table 5, entries 1/2 at 723 K, entries 3/4, and 9/10 at 823 K). However, when the temperature of calcination goes from 723

TABLE 3
Influence of the Methanol-to-Oil Molar Ratio for NaCs(34)X Catalyst[a]

Molar methanol-to-oil ratio	Conversion (%)	Selectivity (%)	Ester molar fraction (%)
15	—	—	Traces
30	—	—	2
50	—	—	18
75	16	95	35
275	55	94	82

[a] 0.5 g of catalyst, 5 g of rapeseed oil, 22 h of reaction time at methanol reflux.

TABLE 4
Transesterification of Rapeseed Oil with Methanol in the Presence of the KW2200 Hydrotalcite (entries 1 and 2) and NaCs(34)X Zeolite (entry 3)[a]

Entry	Conversion (%)	Selectivity (%)	Ester molar fraction (%)	Mass balance (%)
1	12.5	89	33	88
2	34	94	65	86
3	70	96	88	96

[a] 0.5 g of catalyst, 63 mL of methanol, 5 g of rapeseed oil, methanol-to-oil molar ratio of 275, 22 h of reaction time at methanol reflux.

TABLE 5
Transesterification of Rapeseed Oil with Methanol in the Presence of Magnesium Oxide[a,b]

Entry	Calcination	Methanol-to-oil ratio	Time (h)	Ester molar fraction (%)	Conversion (%)	Selectivity (%)	Mass balance (%)
1	Air, 723 K	75	22	88	65	98	91
2	N_2, 723 K	75	22	94	69	99	91
3	Air, 823 K	75	1	58	35	84	94
4	N_2, 823 K	75	1	67	37	97	96
5	N_2, 823 K	75	1	55	27	99	94
6	N_2, 823 K	30	1	40	16	99	90
7	N_2, 823 K	15	1	38	15	100	92
8	N_2, 823 K	15	1	18	6	98	57
9	Air, 823 K	6	1	25	9	97	93
10	N_2, 823 K	6	1	17	7	99	80

[a] 0.5 g of catalyst, 5 g of rapeseed oil, methanol-to-oil molar ratio from 6 to 75, reaction time from 1 to 22 h, at methanol reflux.
[b] Entries **5** and **8**: addition of glycerol (5.2 wt%).

to 823 K, the reaction time is reduced from 22 to 1 h, and the corresponding oil conversion is only reduced by a factor of 2 (Table 5, entries 1/3 or 2/4). Such effect of the calcination temperature on the reactivity has already been reported in the literature for the dimerization of methylcrotonate (10).

In terms of catalytic performance compared to the Cs-exchanged NaX catalyst under the same experimental conditions (methanol-to-oil ratio of 75 and reaction time of 22 h), MgO is far more active than the NaCs(34)X faujasite, 16% of conversion for the NaCs(34)X faujasite (Table 3), and 65–69% for MgO calcined at 723 K (Table 5, entries 1 or 2).

As far as the temperature of calcination had an important effect on the oil conversion, a reaction time of 1 h was used for further experiments (Table 5, entries 3 to 10).

Influence of the methanol-to-oil molar ratio. As for the Cs-exchanged NaX zeolites, a decrease in the methanol-to-oil molar ratio from 75 to 6 leads to a decrease in the conversion, but a high selectivity in esters is maintained (Table 5).

Addition of glycerol. Glycerol was assumed to be responsible for the absence of reactivity of Cs-exchanged NaX faujasites up to a methanol-to-oil molar ratio of about 30. In the case of magnesium oxide, this effect is no longer observed. Glycerol (5.2 wt%) corresponding to the amount of glycerol formed at ≈50% of oil conversion was then added to the starting feed. As shown in Table 5, entries 4 and 5, the conversion of rapeseed oil is effectively lowered for a methanol-to-oil ratio of 75, but slightly less than for a methanol-to-oil ratio of 15 (Table 5, entries 7 and 8). The occurrence of mass transport limitation phenomena cannot be ruled out as it was already reported in the literature (11).

Barium hydroxide. Barium hydroxide was obtained from dehydration of the octahydrate form by calcination overnight at 473 K under reduced pressure (7,12). Under those calcination conditions, the catalytic activity would go through a maximum (7), but the nature of the active species would be $Ba(OH)_2$ in the bulk and $Ba(OH)_2$, H_2O on the surface (12). The experimental results obtained from the reaction of 5 g of rapeseed oil, 0.5 g of catalyst, a methanol-to-oil molar ratio of 6, methanol reflux, 700 rpm, and over a 1-h period, are highly relevant (81% of oil conversion, 97% of selectivity to methyl esters, and 96% of ester molar fraction). These results also clearly show that barium hydroxide is by far more active than magnesium oxide (for comparison, see Table 5, entries 9 or 10) under the same operating conditions which are now close to those used industrially with homogeneous catalysts.

Among the different catalytic systems used in this work to perform the transesterification of rapeseed oil with methanol in the presence of solid basic catalysts, it is confirmed that strong basic properties are required to perform this reaction. Cation-exchanged zeolites are then not really appropriate, whereas systems in the form of a simple oxide with a high surface area show some interesting performances. But the most relevant system is barium hydroxide, which reduces in a very significant manner the operating conditions, thus showing performances close to those of the homogeneous catalysts used industrially.

ACKNOWLEDGMENTS

ONIDOL (Paris, France) is gratefully acknowledged for financial support and Kyowa for a generous gift of KW 2200 catalyst.

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[Received April 23, 2001; accepted September 28, 2001]