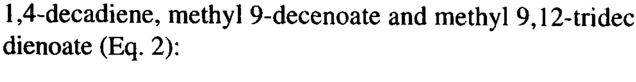
Ethenolysis of Esters of Vegetable Oils: Effect of B_2O_3 Addition To $Re_2O_7/SiO_2.Al_2O_3$-$SnBu_4$ and $CH_3ReO_3/SiO_2.Al_2O_3$ Metathesis Catalysts

Dalmo Mandelli, Marcelo J.D.M. Jannini, Regina Buffon, and Ulf Schuchardt*
Instituto de Quimica, Universidade Estadual de Campinas, 13083-970, Campinas, SP, Brazil

ABSTRACT: Impregnation of $SiO_2.Al_2O_3$ (24.3% Al_2O_3) with 6% B_2O_3 increases the activity of supported Re_2O_7 in the ethenolysis of methyl oleate, but reduces the activity of CH_3ReO_3 on the same support. $Re_2O_7/SiO_2.Al_2O_3/B_2O_3$-$SnBu_4$ is shown to be an effective catalyst for the ethenolysis of methyl linoleate and of the methyl esters of olive oil, and can be recycled after calcination at least five times without loss of activity.
JAOCS 73, 229–232 (1996).

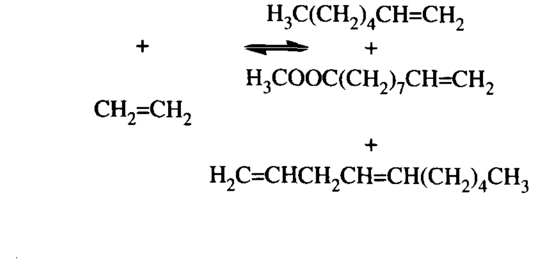
KEY WORDS: B_2O_3 addition, ethenolysis, metathesis, methyltrioxorhenium, rhenium oxide, silica–alumina, vegetable oils.

The cross metathesis of methyl oleate and ethene yields methyl 9-decenoate and 1-decene (Eq. 1):



$$\begin{array}{ccc} H_3C(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 & & H_3COOC(CH_2)_7CH{=}CH_2 \\ + & & + \\ CH_2{=}CH_2 & \rightleftharpoons & H_3C(CH_2)_7CH{=}CH_2 \end{array} \quad [1]$$

These products find application in the manufacture of materials for the chemical industry, such as surfactants, lubricants and polymers (1). Methyl oleate is easily obtained from the transesterification of vegetable oils. Methyl linoleate, present in many vegetable oils in minor amounts, yields 1-heptene, 1,4-decadiene, methyl 9-decenoate and methyl 9,12-tridecadienoate (Eq. 2):



$$\begin{array}{ccc} & & H_2C{=}CHCH_2CH{=}CH(CH_2)_7COOCH_3 \\ & & + \\ H_3C(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOCH_3 & & \\ & & H_3C(CH_2)_4CH{=}CH_2 \\ + & \rightleftharpoons & + \\ & & H_3COOC(CH_2)_7CH{=}CH_2 \\ CH_2{=}CH_2 & & \\ & & + \\ & & H_2C{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \end{array} \quad [2]$$

These transformations open the possibility of achieving materials from vegetable oils which are normally obtained from petroleum. The Re_2O_7/Al_2O_3-SnR_4 catalyst system, used in the metathesis of functionalized olefins, is more active when modified with MoO_3, WO_3, or V_2O_5 (2). Modification of the surface by addition of boric (3) or phosphoric acids (4) also increases the catalytic activity. On the other hand, replacement of alumina by silica–alumina causes a large improvement in the performance of such systems (5). A further improvement can be achieved by utilization of a boric-modified silica–alumina (6). Such improvements in the catalytic activity are usually correlated to an increase in the Brønsted acidity of the resulting system (7).

Re_2O_7 and $SnMe_4$ are effective as catalyst and activator, respectively, in olefin metathesis. Herrmann *et al.* (8) reacted them in refluxing tetrahydrofuran (THF), obtaining methyltrioxorhenium (CH_3ReO_3). In solution, CH_3ReO_3 is only active in the presence of a Lewis acid (for instance, $AlCl_3$) and an alkylating agent (for instance, $SnBu_4$) (8), but when supported on alumina, silica–alumina, or niobia (9–11), its activity in metathesis of acyclic olefins is similar to that of supported Re_2O_7-$SnBu_4$. However, there are few studies in the literature comparing the systems $Re_2O_7/SiO_2.Al_2O_3$-SnR_4 and $CH_3ReO_3/SiO_2.Al_2O_3$ (9). Furthermore, the real effect of the B_2O_3 on the catalyst has not been clarified in a satisfactory way. We have, therefore, studied the catalytic activity of both Re_2O_7 and CH_3ReO_3 supported on $SiO_2.Al_2O_3$ (13 and 24.3% Al_2O_3), in the presence and in the absence of B_2O_3 (6%), for the ethenolysis of methyl oleate. The efficiency of the catalysts $Re_2O_7/SiO_2.Al_2O_3$-$SnBu_4$ and $Re_2O_7/SiO_2.Al_2O_3/B_2O_3$-$SnBu_4$ were verified by comparing their turnover numbers in five consecutive catalytic cycles. The $Re_2O_7/SiO_2.Al_2O_3/B_2O_3$-$SnBu_4$ catalyst was employed for the ethenolysis of methyl linoleate and of the methyl esters obtained in the transesterification of palm and olive oil with methanol.

EXPERIMENTAL PROCEDURES

Materials. Re_2O_7 (99.9%; Fluka, Buchs, Switzerland), NH_4ReO_4 (Fluka 99.9%), H_3BO_3 (99.8%; Merck, Darmstadt, Germany), $SnBu_4$ (Fluka 98%), methyl yellow (99%;

---

*To whom correspondence should be addressed at Instituto de Quimica, Universidade Estadual de Campinas, P.O. Box 6154, 13083-970, Campinas, SP, Brazil.

Aldrich, Milwaukee, WI), octane (Aldrich 99%), and ethene (99.9%; Petroquímica União, Santo André, SP, Brazil) were used without further purification. THF (Merck 99%), benzene (Merck 99.9%), and *n*-hexane (99%; Grupo Química, Penha, RJ, Brazil) were distilled over Na/benzophenone and stored in Schlenk tubes over 4 Å molecular sieve (Fluka). Silica–alumina was obtained from Akzo (Amsterdam, The Netherlands) (24.3% Al_2O_3, pore volume 0.91 cm^3/g and surface area 374 m^2/g) and Strem (Newburyport, MA) (13% Al_2O_3, pore volume 0.78 cm^3/g, surface area 337 m^2/g). Methyl oleate (Aldrich 99%) was treated with basic Al_2O_3 (activated under air and nitrogen at 550°C), potassium carbonate (dried at 270°C), and stored under argon over activated siliça–alumina. Olive oil (Simão Com. Ind. & Cia. Ltda., Alferrade, Portugal) and palm oil (Agropalma Ltda., Belém, PA, Brazil) were transesterified with methanol, using guanidine as catalyst (12), and were treated and stored as described for methyl oleate.

Preparation of the catalysts. The Re_2O_7 catalysts were prepared by pore-volume impregnation of $SiO_2.Al_2O_3$ with an aqueous solution of NH_4ReO_4 and dried overnight at 100°C. The catalysts modified with B_2O_3 (6%) were previously impregnated with an aqueous solution of H_3BO_3, dried and calcined in an air stream at 470°C for 3 h. CH_3ReO_3 was prepared and characterized according to the literature (13).

Ethenolysis. The catalyst precursor (1%) $Re_2O_7/SiO_2.Al_2O_3$ (200 mg) was activated in an air stream (60 mL/min) at 480°C in order to avoid possible loss of rhenium at higher temperatures. After 2 h, the air was replaced by N_2 and the system cooled to room temperature. The catalyst was transferred to a 13-mL teflon-lined stainless-steel autoclave and heated to 50°C under an argon atmosphere. Three mL of a hexane solution containing $SnBu_4$ (1.4 μL, 4.6 μmol), octane (0.1 mL, 0.61 mmol) (internal standard), and methyl oleate (0.49 mL, 1.45 mmol) or methyl linoleate (0.49 mL, 1.45 mmol) were added ([ester]/[Re]/[Sn] ≅ 175:1:0.56). The system was closed, pressurized with ethene (30 bar), and stirred at 50°C for 30 min. This procedure also was used for the reactions with methyl esters of vegetable oils.

In the preparation of the (1%) $CH_3ReO_3/SiO_2.Al_2O_3$ catalysts, 200 mg of $SiO_2.Al_2O_3$ or $SiO_2.Al_2O_3/B_2O_3$ (6%) were activated and transferred to the autoclave. A solution of CH_3ReO_3 (2.1 mg, 8.4 μmol Re) in hexane was then added. The reactions were performed as described previously.

The products were analyzed by gas chromatography (GC) and GC/mass spectrometry (MS). The results are given in wt%, using normalization corrected by the internal standard. The catalytic activities were compared by using a 2^3 factorial design (14). The variables studied were: "active phase" (Re_2O_7 or CH_3ReO_3), "silica–alumina" (13 and 24.3% of Al_2O_3), and "B_2O_3" (presence or absence). In the recycling experiments, 2 g of used (1%) $Re_2O_7/SiO_2.Al_2O_3$ (24.3%)/(6%) B_2O_3-$SnBu_4$ catalyst was calcined at 550°C in an air stream for 6 h. The ethenolysis reaction was then performed as described previously.

Characterization. The total acidity of the (1%) $Re_2O_7/SiO_2.Al_2O_3$ and (1%) $Re_2O_7/SiO_2.Al_2O_3$/(6%) B_2O_3 catalysts, as well as of the $SiO_2.Al_2O_3$ supports, was determined by titration with a benzene solution of *n*-butylamine using methyl yellow as indicator (pK_a = 3.3) (15). Ultrasound was used to accelerate the reactions. The superficial areas were obtained by the BET technique (Micrometrics Flowsorb II 200, N_2, and He; Micrometrics, Norcross, GA).

RESULTS AND DISCUSSION

The type of active compound (CH_3ReO_3 and Re_2O_7), the effect of B_2O_3 (6%) addition, and the alumina content in the support (13 and 24.3% Al_2O_3) were evaluated using a 2^3 factorial design. The conversions of methyl oleate are shown in Figure 1.

The principal products obtained are 1-decene (typically 35%) and methyl 9-decenoate (typically 45%). The remaining 20% are the self-metathesis products 9-octadecene and dimethyl 9-octadecenedioate-1,18. In agreement with results obtained in the self-metathesis of methyl oleate (16), catalysts supported on silica–alumina (24.3% Al_2O_3) show better activity. However, the systems show different behavior with respect to the B_2O_3 addition. There is a negligible effect for both catalysts using silica–alumina with 13% Al_2O_3. Using silica–alumina (24.3% Al_2O_3), the catalysts show an ambiguous behavior—conversion increases for $Re_2O_7/SiO_2.Al_2O_3$, but decreases for $CH_3ReO_3/SiO_2.Al_2O_3$. Warwel *et al.* (10) also found that the addition of B_2O_3 to silica–alumina with 13% Al_2O_3 has no effect on the catalytic activity of $CH_3ReO_3/SiO_2.Al_2O_3$ in the co-metathesis of octene and methyl undecenoate. On the other hand, using a silica–alumina with 60% Al_2O_3, they observed an increase in the cat-

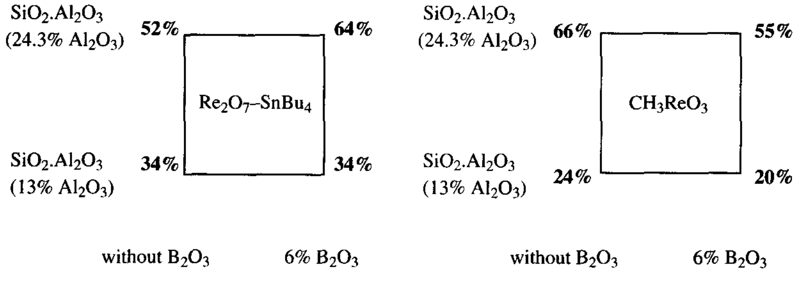


FIG. 1. Conversion of methyl oleate (50°C, 30 bar of ethene, 30 min, [Ole]/[Re] = 175/1, standard deviation 2%).

alytic activity of CH_3ReO_3 after B_2O_3 addition to the support. This shows that the effect of B_2O_3 addition depends strongly on the alumina content of the support.

The conversion (64%) obtained with (1%) $Re_2O_7/SiO_2.Al_2O_3$ (24.3%)/B_2O_3 (6%) corresponds to a turnover number (TN) of 112 ([oleate]/[Re] = 175). Sibeijn and Mol (17) achieved a conversion of 70% for [oleate]/[Re] = 120 (TN 84) in the same reaction, using unmodified catalyst (3%) $Re_2O_7/SiO_2.Al_2O_3$ (24.3%). Using methyl linoleate, we observed a conversion of 50% (TN 87) under the same conditions and obtained 1-heptene (12%), 1,4-decadiene (17%), methyl 9-decenoate (30%), and methyl 9,12-tridecadienoate (22%) as principal products. The remaining 19% were self-metathesis and secondary ethenolysis products. 1,4-Pentadiene was not detected. The same principal products were observed by Ahamad *et al.* (18) in the ethenolysis of methyl linoleate using $SnMe_4$-WCl_6/linoleate in a 1:10 (w/w) ratio. Warwel and Jägers (6) described the most active system, (4.4%) $Re_2O_7/SiO_2.Al_2O_3$ (60% Al_2O_3)/B_2O_3 (5.8%), which allows a conversion of 87% for [ester]/[Re] = 400 (TN 350) in the co-metathesis of butene, pentene, or hexene with methyl esters of palm oil.

The increase of activity observed for (1%) $Re_2O_7/SiO_2.Al_2O_3$ (24.3%)/B_2O_3 (6%) might be explained by the higher acidity of this catalyst (907 μmol/g) compared to 815 μmol/g observed for the B_2O_3-free catalyst. On the other hand, the surface area is slightly reduced (from 374 g/cm^2 to 358 g/cm^2). Although B_2O_3 addition also increases the acidity of the support (from 597 to 820 μmol/g), the activity of $CH_3ReO_3/SiO_2.Al_2O_3$ (24.3% Al_2O_3) is reduced. However, this seems to be true only for silica–alumina with 24.3% Al_2O_3; this effect is not observed for other alumina contents (10).

The $Re_2O_7/SiO_2.Al_2O_3/B_2O_3$-$SnBu_4$ catalyst was used in the ethenolysis of methyl esters of olive and palm oil (Table 1). The catalyst showed a good activity for olive oil (TN 70). The results for palm oil (TN 42) were less favorable due to the high content of saturated esters. The conversion of methyl linoleate in these oils was always higher than that of methyl oleate, which may be due to the higher probability of two double bonds to react. The ethenolysis products observed correspond to those obtained in the ethenolysis of pure methyl oleate and linoleate.

The catalysts (1%) $Re_2O_7/SiO_2.Al_2O_3$ (24.3%)/B_2O_3 (6%) and (1%) $Re_2O_7/SiO_2.Al_2O_3$ (24.3%) were recycled five times without significant loss of activity. The better performance of the B_2O_3-containing catalyst is maintained in the recycling experiments, allowing a total TN above 500. On the other hand, a major drawback of the $CH_3ReO_3/SiO_2.Al_2O_3$ (24.3%) catalyst is that it cannot be easily recycled.

TABLE 1

Composition of Methyl Esters of Olive and Palm Oil Before and After Ethenolysis Using (1%) $Re_2O_7/SiO_2.Al_2O_3$ (24.3%)/B_2O_3 (6%)-$SnBu_4$[a]

Composition	Olive oil		Palm oil	
(wt%)	Before	After	Before	After
1-Heptene	-	0.8	-	1.1
1-Octene	—	0.5	-	0.2
1.4-Decadiene	-	0.9	-	1.5
1-Decene	—	13.5	—	7.3
$C_{9:1}$ ester	—	1.0	—	0.6
$C_{10:1}$ ester	—	15.0	—	8.4
$C_{12:1}$ ester	—	0.8	—	—
$C_{13:2}$ ester	—	1.6	—	1.8
$C_{14:0}$ ester	0.4	0.4	0.8	0.8
9-Octadecene	—	2.6	—	0.9
$C_{16:1}$ ester	1.0	0.6	—	—
$C_{16:0}$ ester	15.5	15.3	37.0	36.7
$C_{18:2}$ ester	6.7	0.6	11.9	3.0
$C_{18:1}$ ester	71.6	37.8	43.0	28.9
$C_{18:0}$ ester	4.5	4.7	7.2	7.3
$C_{20:0}$ ester	0.3	0.3	0.2	0.2
$C_{18:1}$ diester	—	3.5	—	1.1

[a] [Ester]/[Re] ≅ 175, 30 bar of ethene, 50°C for 30 min.

ACKNOWLEDGMENTS

This work was financed by FINEP (Financiadora de Estudos e Projetos), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), and FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo). The authors thank Prof. Dr. R.E. Bruns for helpful discussions.

REFERENCES

1. Streck, R., Olefin Metathesis in Industry—A Status Report, *J. Mol. Catal. 46*:305–316 (1988).
2. Xiaoding, S., P. Imhoff, G.C.N. van den Aardweg, and J.C. Mol, Mixed-Oxide Catalysts for the Metathesis of Functionalized Alkenes, *J. Chem. Soc., Chem. Commun.*, 273–275 (1985).
3. Xiaoding, X., C. Boelhouwer, J.I. Benecke, D. Vonk, and J.C. Mol, $Re_2O_7/Al_2O_3.B_2O_3$ Metathesis Catalyst, *J. Chem. Soc., Faraday Trans. 1 82*:1945–1953 (1986).
4. Sibeijn, M., R. Spronk, J.A.R. van Veen, and J.C. Mol, IR Studies of Re_2O_7 Catalysts Supported on Alumina and Phosphated Alumina, *Catal. Lett. 8*:201–208 (1991).
5. Xiaoding, X., and J.C. Mol, $Re_2O_7/SiO_2.Al_2O_3$-SnR_4 or -PbR_4, a Highly Active Catalyst for the Metathesis of Functionalized Alkenes, *J. Chem. Soc., Chem. Commun.*, 631–633 (1985).
6. Warwel, S., and H.G. Jägers, Middle Chain Fatty Acid Esters from Palm Oil by Olefin Metathesis, *Proceedings of the World Conference on Oleochemicals*, American Oil Chemists' Society, Champaign, 1991, pp. 319–322.
7. Xiaoding, X., C. Boelhouwer, and J.C. Mol, Surface Acidity of Some Re_2O_7-Containing Metathesis Catalysts, *J. Chem. Soc., Faraday Trans. 1 82*:2707–2718 (1986).
8. Herrmann, W.A., J.G. Kuchler, J.K. Felixberger, E. Herdtweck, and W. Wagner, Methylrhenium Oxides: Synthesis from Re_2O_7 and Catalytic Activity in Olefin Metathesis, *Angew. Chem., Int. Ed. Engl. 27*:394–396 (1988).
9. Herrmann, W.A., W. Wagner, U.N. Flessner, Y. Volkhardt, and H. Komber, Methyltrioxorhenium as Catalyst for Olefin Metathesis, *Ibid. 30*:1636–1638 (1991).
10. Warwel, S., M. Harpersheid, and H.G. Jägers, Rheniumkatalysatoren für die Metathese von Olefinen und funktionalisierten Olefinen, Ger. Offen. DE 4,107,056 (1992).
11. Buffon, R., A. Auroux, F. Lefebvre, M. Leconte, A. Choplin, J.M. Basset, and W.A. Herrmann, A Surface Organometallic Approach to the Synthesis of Rhenium-Based Catalysts for the Metathesis of Olefins: CH_3ReO_3/Nb_2O_5, *J. Mol. Catal. 76*:287–295 (1992).

12. Schuchardt, U., and O.C. Lopes, Novos Catalisadores para Transesterificação de Óleos Vegetais, *Proceedings of the II Seminário Brasileiro de Catálise*, Brazil, 1983, pp. 207–219.
13. Herrmann, W.A., J.G. Kuchler, G. Weichselbaumer, E. Herdtweck, and P. Kiprof, Mehrfachbindungen zwischen Hauptgruppenelementen und Übergangsmetallen. LXIV. Methyl(trioxo)rhenium: Basenaddukte und Basenreaktionen. Kristallstruktur von [Natrium(benzo-15-krone-5)]-perrhenat, *J. Organomet. Chem. 372*:351–370 (1989).
14. Box, G.E.P., W.G. Hunter, and J.S. Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building*, John Wiley & Sons, New York, 1978.
15. Johnson, O., Acidity and Polymerization Activity of Solid Acid Catalysts, *J. Phys. Chem. 59*:827–831 (1955).
16. Sibeijn, M., and J.C. Mol, Activity of Supported Re_2O_7 Catalysts for the Metathesis of Methyl Oleate, *Appl. Catal. 67*:279–295 (1991).
17. Sibeijn, M., and J.C. Mol, Ethenolysis of Methyl Oleate over Supported Re-Based Catalysts, *J. Mol. Catal. 76*:345–358 (1992).
18. Ahamad, F.B.H., M.A. Yarmo, and A. Alimuniar, Co-Metathesis Reaction of Methyl Linoleate with Ethene over WCl_6 Catalyst, *Ibid. 89*:357–364 (1994).

[Received June 2, 1995; accepted October 12, 1995]