Hydrogenation of Oleic Acid to 9-Octadecen-1-ol with Rhenium-Tin Catalyst

Thin-Sue Tang[a], **Kien-Yoo Cheah**[a], **Fujio Mizukami**[b,*], **Shu-ichi Niwa**[b], **Makoto Toba**[b] and **Yuen-May Choo**[a]

[a]Palm Oil Research Institute of Malaysia, 50720 Kuala Lumpur, Malaysia and [b]National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

A new supported bimetallic catalyst, rhenium-tin, is able to reduce oleic acid to 9-octadecen-1-ol (*cis* and *trans* isomers) with appreciable yield under mild hydrogenation conditions. This paper reports investigations on the effects of catalyst preparation methods, types of support, catalyst raw materials, mole ratio of the metals, activation and reaction conditions on the activity and selectivity of the catalyst. Catalyst derived from the combination of ammonium perrhenate and stannic chloride on alumina gave the best performance, and the presence of tin in the catalyst is essential for the preservation of the olefinic bond of the oleic acid during hydrogenation.

KEY WORDS: **Hydrogenation, 9-octadecen-1-ol, oleic acid, rhenium-tin catalyst.**

Fatty alcohol is an important chemical in the manufacture of plasticizers and surfactants. The current industrial process for production of fatty alcohols from natural oils and fats is mainly *via* catalytic hydrogenation of fatty acids or their methyl esters. Conventional technology uses copper chromite- or zinc chromate-based catalysts (1–4), and the manufacturing process requires high pressures (20–30 MPa) and temperatures (250–300°C). Furthermore, only saturated alcohol is produced from unsaturated acid with these catalysts.

Oleyl alcohol is an important material for the manufacture of heavy-duty liquid detergents, cosmetics, pharmaceuticals, toiletries, special plasticizers and antifoaming agents (5). It is currently produced by high-pressure hydrogenation of oleic acid with catalysts such as cadmium oxide-chromite-alumina (6) and zinc chromate (2,7).

Yoshino and others (8) reported that rhenium-osmium catalyst with thiophene as an additive could hydrogenate hexanoic and decanoic acids to their corresponding alcohols at 2.5–10.0 MPa hydrogen pressures and at temperatures of 100–130°C. Recent work by Narasimhan *et al.* (9–11) showed that a catalyst system consisting of a ruthenium-tin-boron combination could selectively hydrogenate methyl oleate to oleyl alcohol and methyl palmitate to cetyl alcohol at pressure of 4.4 MPa and temperature of 270°C. The use of rhenium as an excellent catalyst for hydrogenation of long-chain fatty acids at 16.3–26.8 MPa pressures and 137–265°C was reported by Broadbent *et al.* (12). Other combinations, consisting of palladium-rhenium (13) and rhodium-tin (14), have also been used for similar reactions. The inclusion of tin in the catalyst system modified the activity and selectivity of the final catalyst (11,14).

In an earlier paper (15), we reported the development of a new ruthenium-tin-alumina catalyst, prepared by an improved sol-gel method, which could selectively hydrogenate oleic acid to 9-octadecen-1-ol at low pressure (5.6 MPa) and at a temperature of 250°C. Under such mild conditions, a conversion greater than 80% was achieved, with selectivities of unsaturated and total (unsaturated and saturated) alcohols at 81 and 97%, respectively.

In this paper, we report the development of yet another catalyst, rhenium-tin, which could also hydrogenate oleic acid to 9-octadecen-1-ol at a low pressure of 5.6 MPa and 250°C with appreciable yields.

EXPERIMENTAL PROCEDURES

Complexing agent-assisted sol-gel (chemical mixing) method. The rhenium-tin supported catalysts were prepared by the complexing agent-assisted sol-gel (chemical mixing) method as described before (15). Rhenium chloride ($ReCl_3$) and ammonium perrhenate (NH_4ReO_4) were used as the sources of rhenium. Sources of tin were from stannous chloride hydrate ($SnCl_2 \cdot 2H_2O$), stannic chloride hydrate ($SnCl_4 \cdot nH_2O$) and stannic tetraethoxide [$Sn(OC_2H_5)_4$]. Raw materials of supports of catalysts were aluminum isopropoxide [$Al(O\text{-}iso\text{-}C_3H_7)_3$], tetraethoxysilane [$Si(OC_2H_5)_4$], zirconium *n*-propoxide [$Zr(O\text{-}n\text{-}C_3H_7)_4$] and titanium isopropoxide [$Ti(O\text{-}iso\text{-}C_3H_7)_4$].

In the preparation of rhenium-tin-silica catalyst, 1,2-ethanediol was used as the solvent. In all other cases, 2-methyl-2,4-pentanediol was used as the solvent. Some typical procedures are described as follows: For the rhenium-tin-alumina catalyst, 0.94 g of $ReCl_3$ was dissolved with heating in 300 mL of ethanol containing 132.8 g of 2-methyl-2,4-pentanediol. Ethanolic solution (300 mL) containing 114.76 g of $Al(O\text{-}iso\text{-}C_3H_7)_3$ and 2.25 g of $SnCl_4 \cdot nH_2O$ were added to the $ReCl_3$ solution. The mixture was stirred for 3 h at 80°C. A homogeneous solution was obtained. Water (46 g) was added to this solution, which was then aged for 1 h at the same temperature. The gel obtained was dried at 170°C under vacuum, and ground. The rhenium-alumina catalyst was prepared in the same manner described above but in the absence of tin compound.

Conventional impregnation method. The alumina and zirconia supports of the impregnation catalysts were first prepared by the sol-gel method similar to that described above by using only $AlO\text{-}iso\text{-}C_3H_7)_3$ and $Zr(O\text{-}n\text{-}C_3H_7)_4$ as raw materials and 2-methyl-2,4-pentanediol as solvent. The impregnation of rhenium and tin onto the alumina support was carried out in the conventional way described below with ethanol as solvent. $ReCl_3$ (1 g) and 2.39 g of $SnCl_4 \cdot nH_2O$ were dissolved in ethanol, and the solution was added to a suitable quantity of Al_2O_3, which has been previously heated under vacuum at 200°C for 2 h and cooled. After stirring for 3 h, the solvent was removed, and the catalyst was dried prior to activation.

Co-precipitation method. $ReCl_3$ (1 g) and 2.39 g of $SnCl_4 \cdot nH_2O$ were dissolved in 20 mL ethanol to give a clear solution. This was mixed with another solution containing 121.7 g of $Al(O\text{-}iso\text{-}C_3H_7)_3$ in 300 mL dioxane at

---

*To whom correspondence should be addressed at Head of Moleular Recognition Lab., Surface Chemistry Dept., National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan.

TABLE 1

Effect of Atomic Ratio of Rhenium to Tin on the Activity and Yield in the Hydrogenation of Oleic Acid[a]

Atomic ratio of Re/Sn	Conversion (%)	Alcohol yield (%)	
		9-Octadecen-1-ol	Total
1:0	100.0	0	57.9
1:2.0	77.7	25.2	40.7
1:3.0	76.6	25.3	35.81

[a]Experimental conditions were as follows: The catalysts were prepared by sol-gel method from $ReCl_3$, $SnCl_4 \cdot nH_2O$ and $Al(O\text{-}iso\text{-}C_3H_7)_3$ with 2-methyl-2,4-pentanediol as solvent. Rhenium metal loading was 2 wt%. The catalysts were activated at 400°C for 4 h in a stream of hydrogen. Reaction conditions: temp., 250°C; pressure, 5.6 MPa; reaction time, 20 h; oleic acid, 50 g and catalyst, 6% by weight. Total alcohol, 9-octadecen-1-ol + stearyl alcohol; other products obtained were mainly hydrocarbons (similar for the rest of the tables).

80°C, resulting in a homogeneous solution. Ammonia solution (160 mL) was added dropwise, and a thick precipitate was obtained. After filtration, the solid was washed with ethanol and dried under vacuum before activation.

Hydrogenation reaction. The hydrogenation reaction was carried out in a 500-mL reactor equipped with a pressure regulator. The reactor was charged with oleic acid together with the catalyst and purged with hydrogen four times at different pressures (1.0, 1.0, 2.0 and 4.0 MPa) to expel air. The reactor was then heated up to the required temperature and pressurized with hydrogen to the required pressure, which was maintained constant throughout the reaction. Stirring was maintained at about 1000 rpm. At the end of the specified time, the reactor was cooled, and the reaction mixture was removed for analysis. Unless otherwise stated, the catalyst was activated prior to usage by heating at 400°C for 4 h in a stream of hydrogen gas.

Analysis of reaction products. The reaction products were analyzed by gas chromatography with a 50 m × 0.25 mm ULBON HR SS-10 column (Shinwa-kako Co. Ltd., Kyoto, Japan) operated with temperature programming from 150–200°C at 2°C/min and with helium as a carrier gas. A flame-ionization detector was used. The fatty acids and fatty alcohols in the product were derived to methyl esters and alkyl acetates, respectively, without prior separation. Prior to the normal methylation step with BF_3/methanol solution, the product mixture was first saponified with a 0.5 N NaOH/methanol solution. For quantitation, heptadecanoic acid was used as an internal standard. The by-products from the hydrogenation reaction were mainly hydrocarbons.

RESULTS AND DISCUSSION

As mentioned in our earlier paper (15), competitive reactions such as isomerization, saturation of the olefinic bond and reduction of carboxylic group can occur during the hydrogenation of oleic acid and lead to the possible formation of elaidic acid, stearic acid, oleyl alcohol (*cis*-9-octadecen-1-ol), elaidyl alcohol (*trans*-9-octadecen-1-ol) and stearyl alcohol. The reaction and catalyst activation conditions play a critical role in determining the yield and composition of the product. Over-hydrogenation often leads to the formation of hydrocarbons. We investigated the factors affecting the performance of the rhenium-tin catalysts, and the results obtained are reported and discussed below.

Effect of atomic ratio of rhenium to tin. Table 1 shows the effect of atomic ratio of rhenium to tin on the catalytic activity and yield for alcohol formation in the hydrogenation of oleic acid. In the absence of tin, the catalyst was highly active and showed a conversion of 100% with total alcohol yield of 57.9%. Only saturated stearyl alcohol was formed, and the other product was stearic acid. The incorporation of tin into the catalyst clearly modified the property of the catalyst, resulting in the formation of some 9-octadecen-1-ol. However, the conversion decreased and so did the total alcohol yield. Under the conditions of the experiment, the atomic ratio of Re/Sn of 1:2 appeared to be the optimum, as further increasing the tin content decreased the activity of the catalyst slightly and also the total alcohol yield. This reduction in alcohol yield could be due to the formation of hydrocarbon because the inclusion of tin suppresses the saturation of olefinic bond and promotes the reduction of the carboxylic group to produce alcohol. However, over-hydrogenation led to further reduction of the $\text{-}CH_2OH$ group to hydrocarbon. A similar observation was made for hydrogenation of oleic acid with ruthenium-tin catalyst, where the high proportion of tin in the bimetallic catalyst (Ru/Sn = 1:3) also resulted in reduction in 9-octadecen-1-ol production and in total alcohol selectivities (15).

Effect of catalyst preparation method. Table 2 shows the effect of catalyst preparation method on the activities

TABLE 2

Effect of Catalyst Preparation Method on the Hydrogenation of Oleic Acid[a]

Catalyst	Preparation method	Conversion (%)	Alcohol yield (%)	
			9-Octadecen-1-ol	Total
Re-Sn-Al_2O_3	Co-precipitation	52.0	20.3	29.3
Re-Sn-Al_2O_3	Impregnation	82.0	28.9	48.3
Re-Sn-Al_2O_3	Sol-gel	77.7	25.2	40.7
Re-Sn-ZrO_2	Sol-gel	35.2	6.2	9.1
Re-Sn-ZrO_2	Impregnation	99.5	9.1	48.6

[a]Catalysts were prepared with $ReCl_3$, $SnCl_4 \cdot nH_2O$, $Al(O\text{-}iso\text{-}C_3H_7)_3$ and $Zr(O\text{-}n\text{-}C_3H_7)_4$ as raw materials and 2-methyl-2,4-pentanediol as a solvent. Alumina and zirconia supports used for impregnation were also prepared by the sol-gel process from their corresponding alkoxides. Impregnation and co-precipitation catalysts were prepared as described in the text. Rhenium loading was 2 wt% and atomic ratio of Re/Sn was 1:2 in all cases. Reaction time, activation and reaction conditions, substrate and catalyst amount were same as in Table 1.

TABLE 3

Effect of Support of Re-Sn Catalyst on Hydrogenation of Oleic Acid[a]

Catalyst	Reaction time (h)	Conversion (%)	Alcohol yield (%)	
			9-Octadecen-1-ol	Total
SiO_2	20	42.2	19.8	25.0
Al_2O_3	20	77.7	25.2	40.2
ZrO_2	20	35.2	6.2	9.1
TiO_2	20	51.4	24.6	31.8

[a] Catalysts were all prepared by sol-gel method described earlier. Sources of rhenium and tin were $ReCl_3$ and $SnCl_4 \cdot H_2O$, respectively. For the supports, the raw materials were their alkoxides. Rhenium loading was 2 wt% and the atomic ratio of Re/Sn was 1:2. Activation and reaction conditions were as in Table 1.

of the Re-Sn catalysts supported on alumina and zirconia and their effect on the yield of alcohols. Re-Sn-Al_2O_3 prepared by the impregnation and sol-gel methods showed comparable performance, with about 80% conversion. Yields of 9-octadecen-1-ol and total alcohol were about 25 to 29% and 41 to 48%, respectively. However, the performance of the corresponding co-precipitation catalyst was much less satisfactory.

For the Re-Sn-ZrO_2 catalyst, the impregnation catalyst gave good performance in achieving 99.5% conversion, but the 9-octadecen-1-ol yield was rather low at 9.1% and the total alcohol yield was 48.6%. The data also indicated that the Re-Sn-ZrO_2 catalyst was poorer than the Re-Sn-Al_2O_3 catalyst in terms of 9-octdecen-1-ol selectivity and thus in yield.

It appeared that rhenium-tin impregnated on alumina and zirconia performed better than catalyst obtained by the sol-gel method. This observation is interesting when compared with that of ruthenium-tin-alumina, where the catalyst from the sol-gel method was superior in activity and selectivity to that from impregnation. However, in the case of ruthenium-tin-zirconia, the sol-gel catalyst, though more active than the impregnated one, showed poorer alcohol selectivities (15).

The rhenium-tin-alumina prepared by the co-precipitation method showed lower activity than catalysts prepared by other methods, which is in contrast to results obtained with ruthenium-tin, where the corresponding catalyst from co-precipitation showed the highest activity but lower alcohol selectivities (15).

Effect of support of Re-Sn catalyst. The effect of the support of the Re-Sn catalyst on the hydrogenation of oleic acid is shown in Table 3. The activity of the catalysts depended on the type of support and decreased in the order alumina > titania > silica > zirconia. However, the yield of 9-octadecen-1-ol decreased also in the order of alumina >titania > silica > zirconia, and the same trend was observed for total alcohol yield. Thus, alumina is the best support for the rhenium-tin catalyst, which is similar to that for ruthenium-tin catalyst (15). Thus, considering both the activity and unsaturated alcohol yield, we chose Re-Sn-Al_2O_3 for most of our investigations.

Effect of catalyst raw material. The effect of catalyst raw material on the hydrogenation of oleic acid was studied by comparing hydrated stannous and stannic chlorides as well as stannic tetraethoxide as sources of tin while rhenium trichloride and ammonium perrhenate were used as sources of rhenium (Table 4). Hydrated tetravalent stannic chloride appeared to promote catalyst activity more than the hydrated divalent stannous chloride and stannic tetraethoxide. Stannic tetraethoxide, however, was better than hydrated stannous chloride in that, though the conversions were comparable, the catalyst derived from stannic tetraethoxide afforded higher yields of both unsaturated alcohol and total alcohol. On the other hand, for rhenium sources, catalyst derived from ammonium perrhenate gave better yield of unsaturated alcohol than that from rhenium chloride. Thus, the catalyst derived from the combination of ammonium perrhenate and stannic chloride hydrate gave the best performance in terms of conversion, unsaturated alcohol and total alcohol yields. This was in contrast to the result obtained earlier (15) with ruthenium-tin-alumina catalyst, where chloride-free catalyst showed the better conversion and selectivity.

Effect of activation condition. Catalyst activation conditions were found to affect the catalytic activity and selectivity (Table 5). For Re-Sn-SiO_2 catalyst, activation of catalyst at 400°C for 4 h in a stream of hydrogen gave better results than when the catalyst was calcined in air at 400°C for 4 h prior to activation. For Re-Sn-Al_2O_3, activating the catalyst at 400°C was better than at 300°C. This was in agreement with our earlier result (15) on ruthenium-tin catalyst, where calcination of the catalyst was also not necessary prior to activation.

Effect of hydrogenation temperature. At temperatures of 150°C or below there was no production of alcohol, and at 200°C the conversion was low at 13.7% and so were the yield of unsaturated and total alcohols (Table 6). At 250°C, the conversion was higher at 77.7%, and the yield of 9-octadecen-1-ol and total alcohol also improved to 25.2 and 40.7%, respectively. Increasing the hydrogenation temperature to 275°C improved the activity, as indicated by higher conversion, but the 9-octadecen-1-ol yield de-

TABLE 4

Effect of Catalyst Raw Materials on Hydrogenation of Oleic Acid[a]

Metal source		Reaction time (h)	Conversion (%)	Alcohol yield (%)	
Re	Sn			9-Octadecen-1-ol	Total
$ReCl_3$	$SnCl_2 \cdot 2H_2O$	20	61.4	19.2	25.5
$ReCl_3$	$SnCl_4 \cdot nH_2O$	20	77.7	25.2	40.2
NH_4ReO_4	$Sn(OC_2H_5)_4$	20	60.7	29.1	39.6
NH_4ReO_4	$SnCl_4 \cdot nH_2O$	20	79.8	36.7	58.4

[a] All catalysts were supported on alumina and were prepared by sol-gel method as described earlier. Rhenium loading was 2 wt% and atomic ratio of Re/Sn was 1:2. Activation and reactions conditions were as in Table 1.

TABLE 5

Effect of Activation Condition of Sol-Gel Re-Sn Catalysts on Hydrogenation of Oleic Acid[a]

Activation condition (°C)	Reaction time (h)	Conversion (%)	Alcohol yield (%)	
			9-Octadecen-1-ol	Total
Re-Sn-SiO_2				
400 Air				
400 H_2	19.1	36.0	8.0	9.4
400 H_2	20.0	42.2	19.8	24.9
Re-Snk-Al_2O_3				
300 H_2	21.0	49.2	13.4	21.0
400 H_2	20.0	77.7	25.2	40.7

[a] Reaction conditions were as in Table 1. Rhenium loading was 2 wt% and the atomic ratio of Re/Sn was 1:2. Activation time was 4 h for all catalysts.

TABLE 6

Effect of Temperature on the Hydrogenation of Oleic Acid with the Sol-Gel Catalysts[a]

Temperature (°C)	Reaction time (h)	Conversion (%)	Alcohol yield (%)	
			9-Octadecen-1-ol	Total
Re-Sn-Al_2O_3				
200	20	13.7	7.8	9.0
250	20	77.7	25.2	40.7
275	20	94.0	8.0	51.1

[a] Rhenium metal loading was 2 wt% and atomic ratio of Re/Sn was 1:2. Activation and reaction conditions were as in Table 1.

TABLE 7

Effect of Pressure on the Hydrogenation of Oleic Acid with the Sol-Gel Catalyst[a]

Pressure (MPa)	Reaction time (h)	Conversion (%)	Alcohol yield (%)	
			9-Octadecen-1-ol	Total
3.0	21.0	65.8	28.4	43.7
5.6	20.0	77.0	25.2	40.7
8.0	20.7	69.9	21.7	37.0

[a] Re-Sn-Al_2O_3 was used. Rhenium loading was 2 wt% and atomic ratio of Re/Sn was 1:2. Catalysts were prepared from $ReCl_3$ and $SnCl_4 \cdot nH_2O$. Amount of catalyst used was 6%. The reaction temperature was 250°C, and activation was as in Table 1.

creased markedly to only 8.0%, while the total alcohol increased to 51.1%. This indicated that, at 275°C, hydrogenation of the double bond predominated. This differed from our earlier result on ruthenium-tin catalyst from nonchloride sources where at 275°C, though the conversions were high (15), the unsaturated and total alcohol selectivities were significantly lower (than those at lower hydrogenation temperatures), indicating possible overhydrogenation to hydrocarbons.

Effect of hydrogenation pressure. The effect of pressure on hydrogenation of oleic acid with rhenium catalyst was not significant, as can be seen in Table 7. The reaction appeared to be optimum at pressures of 5.6 to 8.0 MPa as the conversion and product yield at these pressures were quite close to one another. The fact that the hydrogenation was not much affected by hydrogen pressure indicated that the reaction rate was of zero order for hydrogen pressure above 3.0 MPa. Our earlier results showed that for the ruthenium-tin catalyst, the effect of pressure depended on the raw materials of the catalyst. For ruthenium-tin catalyst derived from chloride sources, the effect of pressure was not significant, whereas for the catalyst derived from chloride-free sources, the activity of the catalyst increased with pressure and yet maintained the 9-octadecen-1-ol and total alcohol selectivities.

Role of tin. From the results shown above, it was evident that supported rhenium-tin catalyst could hydrogenate oleic acid to a mixture of 9-octadecen-1-ol and stearyl alcohol with appreciable yield and that the presence of tin was essential for the formation of 9-octadecen-1-ol. The role of tin in bimetallic catalysts, such as platinum-tin in cracking reactions (16), platinum-tin-nylon in the hydrogenation of α,β-unsaturated aldehydes (17–19), ruthenium-tin in the hydrogenation of olefinic double bonds and carbonyl groups and ruthenium-tin-boron for hydrogenation of fatty esters to their corresponding alcohols (9–11), has been reviewed in our earlier paper (15). Basically, the tin in the catalyst system interacts with the principal metal (Pt, Ru, as the case may be) in such a way that it activates the more polar carbonyl group. With respect to the double bond, the tin also serves to decrease the relative number of principal metal on the surface of the catalyst, thus affecting the reactivity of the olefinic group.

In the case of the rhenium-tin catalyst, our earlier proposal about the performance of the ruthenium-tin catalyst, which was attributed to the selective absorption of the >C=C< olefinic bond or the -COOH group of the oleic acid on the catalyst surface under different catalyst compositions and reactions, should also be applicable. When the catalyst system shows stronger affinity for the unsaturated double bond, the saturation reaction will predominate, resulting in the formation of stearic acid. However, if the catalysts have stronger affinity for the carboxylic group, the manner in which the reaction will proceed depends on the degree of adsorption: strong adsorption will result in no hydrogenation, and moderate adsorption will result in selective hydrogenation of the carboxylic group to alcohol.

In the hydrogenation of oleic acid with ruthenium-tin catalyst (15), high conversion and yield of unsaturated alcohol were obtained, indicating that the preservation of double bonds by tin was stronger when incorporated into the ruthenium catalyst. In the case of rhenium, improvement in the preservation of olefinic bonds was relatively of a smaller degree. Yet, the yield could be increased to about 50%. This implied that about an equal amount (*i.e.*, 50%) of the olefinic bonds and carboxylic acid groups were attached to the surface of the rhenium-tin catalyst.

ACKNOWLEDGMENTS

The authors thank the Director General of PORIM and the Director General of NIMC for permission to publish this paper, and also to the Agency of Industrial Science and Technology (AIST), Japan, for supporting this research collaboration.

REFERENCES

1. Adkins, H., and K. Folkers, *J. Am. Chem. Soc. 53*:1091 (1931).
2. Kreutzer, U.R., *J. Am. Oil Chem. Soc. 61*:343 (1984).
3. Adkins, H., and R. Connor, *Organic Reaction 8*:1 (1954).

4. Carduck, F.J., J.F. Falbe, T. Ceckenstein and P. Joachim, *Ger. Offen.*, DE 3624812 (1988).
5. Glasl, J., *Fatty Alcohol—Raw Matrials, Methods, Uses,* Henkel KGaA, Düsseldorf, 1982, p. 121.
6. Komp, H.D., *Ibid.*, p. 49.
7. Demmering, G., *Ger. Offen.*, DE 2513377 (1976).
8. Yoshino, K., Y. Kajiwara, N. Takaishi, Y. Inamota and J. Tsuji, *J. Am. Oil Chem. Soc. 67*:21 (1990).
9. Narasimhan, C.S., V.M. Deshpande and K. Ramnarayan, *Appl. Catal. 48*:L1 (1989).
10. Narasimhan, C.S., V.M. Deshpande and K. Ramnarayan, *Ind. Eng. Chem. 28*:1110 (1990).
11. Narasimhan, C.S., V.M. Deshpande and K. Ramnarayan, *J. Catal. 121*:174 (1990).
12. Broadbent, H.S., G.C. Campbell, W.J. Bartley and J.H. Johnson, *J. Am. Chem. 24*:18 (1959).
13. Snappe, R., and J.P. Bournonville, West German Patent 3217 4299.2 (1982).
14. Travers, C., J.P. Bournonville and P. Martino, *8th International Conference on Catalysis, Vol. III*, edited by T. Pachema, Verlag Chemie Weinheim Deerfield Beach Bond, Berlin, p. 86.
15. Cheah, K.Y., T.S. Tang, F. Mizukami, S. Niwa, M. Toba and T.M. Choo, *J. Am. Oil Chem. Soc. 69*:410 (1992).
16. Burch, R., and L.C. Garla, *J. Catal. 71*:368 (1981).
17. Poltarzewski, Z., S. Galvagno, R. Pietropaolo and P. Staiti, *Ibid. 120*:190 (1986).
18. Galvagno, S., Z. Poltarzewski, A. Donato, G. Neri and R. Pietropaolo, *J. Mol. Catal. 35*:365 (1986).
19. Galvagno, S., A. Donato, G. Neri and R. Pietropaolo, *Catal. Lett. 8*:9 (1991).

[Received November 21, 1992; accepted March 16, 1993]