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Alkylation of Toluene with 2-Propanol over Titania-Silica-Alumina Catalysts

K. V. C. Rao,* K. R. Sabu, and C. G. R. Nair†
Inter Disciplinary Research Group, Vikram Sarabhai Space Centre, Trivandrum-695022, India
†Department of Chemistry, University of Kerala, Trivandrum-695034, India

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The alkylating activity of titania supported on silica-alumina has been reported earlier (V. G. Kumar, T. S. Shoba, and K. V. C. Rao, *Tetrahedron Lett.*, **26**, 3281 (1985)). Further investigations to synthesize such a catalyst with optimum alkylation activity resulted in the coprecipitation of the catalyst from a solution of pH 4—the test reaction selected being the alkylation of toluene with 2-propanol in a fixed bed tubular reactor. The product mixtures at different reaction times are analyzed to have a view on the variation of yields of different alkylated products with reaction time. The alkylated products are *o*-cymene, *p*-cymene, and diisopropyltoluenes (DIT). The presence of titania exerts a synergistic effect upon the alkylating activity of silica-alumina. Also the catalytic activity is governed by the physical characteristics of the catalyst like surface area and porosity. The trend of para-rich isomer distribution observed in the product mixture is attributed to the steric factors. It has been observed that *o*-cymene is formed at a constant rate whereas *p*-cymene formation decreased with reaction time. Increased formation of diisopropyltoluenes are observed with the passing of reaction time. Alkylation studies in the temperature range 165—240 °C have been done to find the effect of reaction temperature on the product distribution. Thus a decrease in the ortho to para molar ratio with increase in reaction temperature and increased formation of diisopropyltoluenes at lower temperatures are observed. No considerable reduction in the alkylation activity has been noticed up to five regeneration cycles.

Conventional catalysts like Lewis acids and mineral acids which are in use for the acid catalyzed alkylation reactions usually result in major corrosion problems due to large amounts of acid vapours.[1,2] Separation of the catalyst from the reaction products also poses difficulty in such homogeneous reactions. The introduction of solid acid catalysts like zeolites was a major breakthrough in alkylation chemistry.[2] Application of high-silica zeolites for alkylation process was realized commercially for the first time by Mobil/Badger[3] in 1980.[2] Crystalline aluminosilicate[4] and silica-alumina[5,6] were previously known to catalyze alkylation reactions. In addition, zeolites are modified by using alkaline earth metals[7] and Group IA,[8] Group IIIA,[9] and Group IVA[10] metals and are used for various alkylation reactions. The sulfates of metals like Zn, Al, Cd, Cu, and Ni supported on silica-alumina are used as catalysts in the alkylation of toluene with methanol of which zinc-sulfate supported on silica-alumina is the most active.[11] Silica-alumina,[12,13] reduced silica-alumina,[14] silica-alumina containing salts of Mn, Zn, Cr, Cu, Cd,[15] molecular sieves,[16] zeolites,[17,18] and rare-earth exchanged zeolites[19] are also used to alkylate benzene with ethylene.

Moreover, combinations of oxides of transition metals[20,21] alone or supported[22] on silica or silica-alumina are used for similar reactions. Certain supported systems like chromia/silica, molybdenum oxide on silica-alumina which are used for oligomerization and polymerization reactions respectively had indicated the utility of supported transition metal catalysts.[23–26] Incorporation of metal oxides may alter the catalytic activity and selectivity to different products.[27] A catalyst containing titanium oxide supported on silica-alumina was reported previously for the alkylation of different aromatic compounds.[28] A wide range of alkylating agents like alcohols, halides, and olefins have been used with this catalyst. The catalyst is reported to be regenerable also.

A systematic synthesis of Tisial catalysts and efficiency of these catalysts in the alkylation of toluene with 2-propanol has been reported in this paper. The catalytic activities of different Tisial catalysts are also compared with that of a synthetic silica-alumina sample. The effect of temperature on the catalytic activity of alkylation, the relative yields of different products and the regeneration studies of the catalyst have also been included.

Experimental

Sodium silicate (Scientific Chemicals), after dissolving in water, is filtered to remove any undissolved sediments. Aluminum sulfate used is of A.R. grade. Titanium tetrachloride is obtained from M/S Travancore Titanium Products, Chavara. Nitric acid and ammonia used are of chemically pure quality.

To an aqueous solution of sodium silicate (260 g dm^{-3} of distilled water) dilute nitric acid (1 : 1) is added at 90 °C under constant agitation, till the pH of the solution is reduced to one. The desired quantity of hot aluminum sulfate solution (333 g dm^{-3}) is added, followed by the addition of titanium tetrachloride (20 ml) under vigorous agitation. Ammonia solution is added slowly, till the required pH is attained. Precipitations are carried out at different pH's (2, 3, 4, 5, 6, 7, 8, and 9) and are designated as Tisial-2, Tisial-3, and so on. Silica-alumina catalyst is also synthesized at pH 4 without titania. The precipitates are washed with distilled water till free from sulfate ion and are extruded as pellets. These are dried at 120 °C for 12 h and sintered at 600 °C and used as catalysts for the alkylation.

The silica to alumina molar ratio as well as titania contents of different catalysts determined by chemical analysis, and physical parameters such as pore volume, surface area etc., are included in Table 1.

The catalyst (25 g which corresponds to 60 ml in volume) is charged to a tubular glass reactor of 2.54 cm diameter. Provision is made to maintain the pre-catalyst, catalyst and post-catalyst zone temperatures at the desired levels. The reactor is fed under gravitational flow at a constant LHSV (liquid hourly space velocity) of 0.5 with a precalibrated capillary tube. The reaction products are collected by condensing the volatiles with chilled water. Samples are withdrawn from the bulk of the rection products at intervals of one hour and analyzed. The duration of each experiment is 7 h except for those done to study the effect of temperature on alkylation reaction, where it is 3 h. Toluene to 2-propanol molar ratio is kept at 3 : 1 in each experiment. To estimate the catalyst life for alkylation, the same catalyst (Tisial-5) is subjected to nine successive regenerations by passing air at the end of each experiment of 7 h at 600 °C.

Product mixtures are analyzed by gas chromatography in a Shimadzu GC-5A gas chromatograph. A stainless steel column (3 mm ϕX2 m) packed with 5% SE 52 on Shimalite 60—80 mesh support is used under the experimental conditions of column temperature 120 °C, injection port temperature 220 °C, detector FID and carrier gas (Helium) flow rate of 60 $\mathrm{cm^3\ min^{-1}}$. A Shimadzu C-RIA data processor was used to calculate the peak areas. Products are found to be *p*-cymene (*p*-isopropyltoluene), *o*-cymene (*o*-isopropyltoluene), and three isomers of diisopropyltoluene (DIT). Percentage yields of alkylaromatics are calculated in the following way.

(i) For cymenes

$$\%\ \text{Yield} = \frac{(\text{No of moles of cymene formed}) \times 100}{\text{No of moles of 2-propanol fed}}$$

(ii) For diisopropyltoluene (DIT):

$$\%\ \text{Yield} = \frac{2 \times (\text{No of moles of DIT formed}) \times 100}{\text{No of moles of 2-propanol fed}}$$

Total Yield = (i) + (ii)

Products are also indentified by bp. Fractional distillation is done in a spinning band distillation column, B/R 36T; Option 3 (B. R. Instrument Coorporation, Maryland USA) at an rpm of 4000 and reflux ratio 20 : 1.

Results and Discussion

The extent of total conversion of 2-propanol to alkylaromatics over various Tisial and silica-alumina catalysts at 200 °C with reaction time is shown in Fig. 1. The conversion to *p*-cymene, *o*-cymene, and diisopropyltoluenes after the end of each hour of the experiment over Tisial-4 catalyst is given in Fig. 2.

Results of the study on regenerability and catalyst life is shown in Fig. 3.

Table 2 gives the mol% of 2-propanol converted to *o*-cymene and *p*-cymene over Tisial-4, Tisial-5, and silica-alumina catalysts.

The temperature dependence of alkylating activity

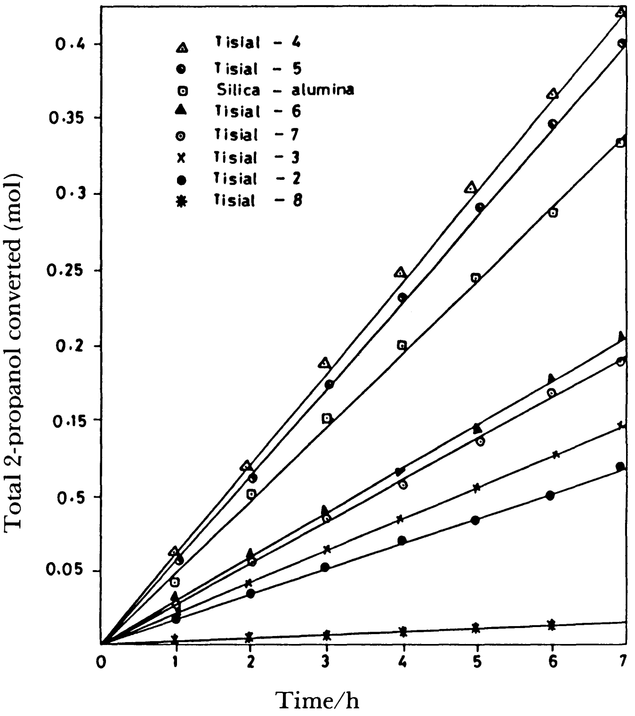


Fig. 1. Comparison of alkylating activity of different catalysts. (The cumulative number of moles of 2-propanol converted to alkylaromatics with reaction time is given.)
Reaction conditions; reaction temperature: 200 °C, LHSV: 0.5, 2-propanol/toluene (mole ratio)=1/3.

Table 1. Physicochemical Characteristics of Tisial Catalysts Precipitated at Different pH

Disignation	pH of co-pptn	SiO_2/Al_2O_3 (molar ratio)	$\%TiO_2$ (by wt)	Pore vol.	Surface area
				$\mathrm{cm^3\,g^{-1}}$	$\mathrm{m^2\,g^{-1}}$
Tisial-2	2	47.6	9.1	0.61	61.7
Tisial-3	3	39.2	10.0	0.68	67.5
Tisial-4	4	16.4	10.4	0.71	100.0
Tisial-5	5	9.0	12.3	0.60	65.5
Tisial-6	6	8.7	11.8	0.50	49.5
Tisial-7	7	8.3	11.1	0.35	46,0
Tisial-8	8	8.2	8.7	0.07	11.5
Tisial-9	9	7.8	8.6	0.03	—
SiO_2-Al_2O_3	4	16.3	—	1.20	135.0

is investigated over Tisial-4 catalyst at different temperatures viz. 165, 180, 200, 220, and 240 °C (Table 3).

The distribution of different components in the product mixture at different temperatures is given in Table 4.

The percentage of titania content varied only mariginally with the pH of coprecipitation, whereas silica to alumina molar ratio decreased drastically from 47.6 (pH=2) to 9 (pH=5) (Table 1) and further increase in pH does not have much effect. Lower pH may be maximizing the silica precipitation whereas precipitation of aluminum hydroxide is favored by higher pH. The surface area and pore volume of the catalyst also indicate an increase up to pH 4 and further a decrease as is evidenced from Table 1. These two physical parameters are considerably diminished by precipitation at higher pH. The conversion of 2-propanol to alkylaromatics over different Tisial catalysts also showed an identical trend, where

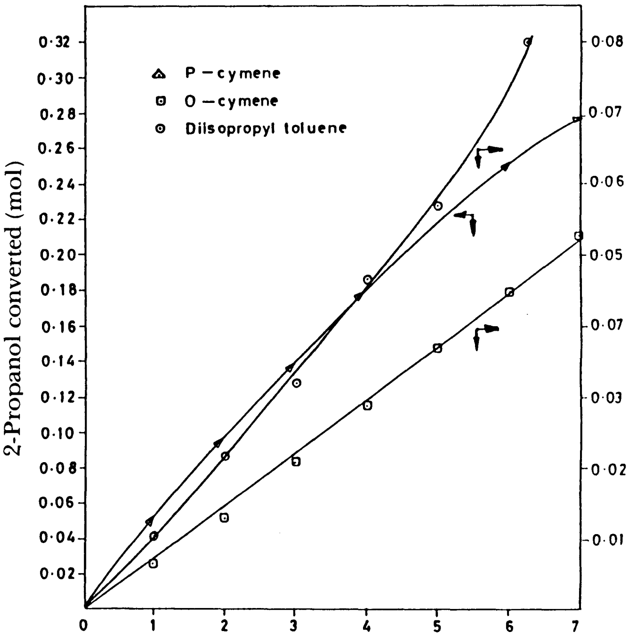


Fig. 2. Cumulative formation of *p*-cymene, *o*-cymene, and diisopropyltoluenes with reaction time over Tisial-4. (The number of moles of 2-propanol converted is given.)
Reaction conditions; reaction temperature: 200 °C, LHSV: 0.5, 2-propanol/toluene (mole ratio)=1/3.

Table 2. The Mole % of 2-Propanol Converted to *o*-Cymene and *p*-Cymene over Tisial-4, Tisial-5, and Silica-Alumina at 200 °C. Reaction Time : 7 h

Catalyst	% of 2-propanol converted;	
	to *o*-cymene	to *p*-cymene
Tisial-4	9.6	52.4
Tisial-5	10.0	46.4
$SiO-Al_2O_3$	9.3	37.3

Table 3. Effect of Temperature on the Alkylation Activity of Tisial-4. Reaction Time: 3 h

Temp	Yield/%				*o*/*p* ratio
°C	*o*-Cymene	*p*-Cymene	DIT	Total	
165	10.0	18.4	16.4	44.8	0.54
180	9.4	22.0	20.8	52.2	0.43
200	9.0	56.0	15.0	80.0	0.16
220	7.3	42.2	13.8	63.3	0.17
240	5.5	39.3	8.8	53.6	0.14

Table 4. Product Distribution (mol%) at Different Temperatures

Temp/°C	Toluene	*o*-Cymene	*p*-Cymene	DIT
165	88.3	3.2	5.9	2.6
180	86.0	3.1	7.2	3.5
200	72.8	2.9	21.5	2.6
220	81.0	2.4	14.4	2.3
240	84.0	1.7	12.6	1.6

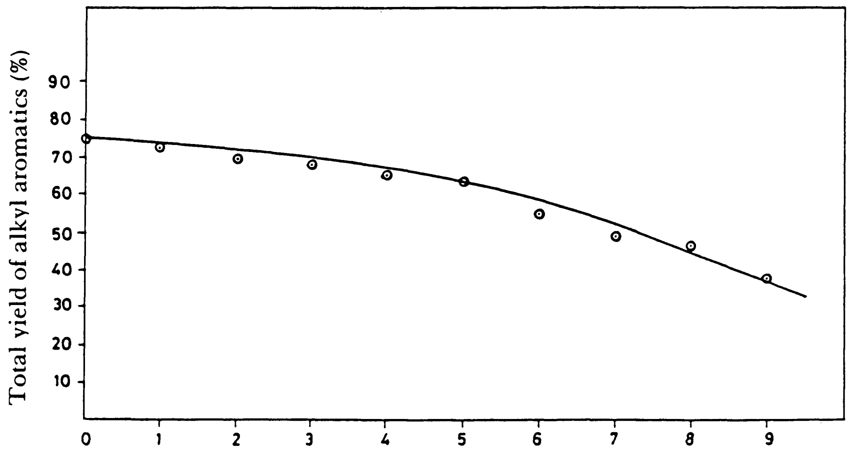


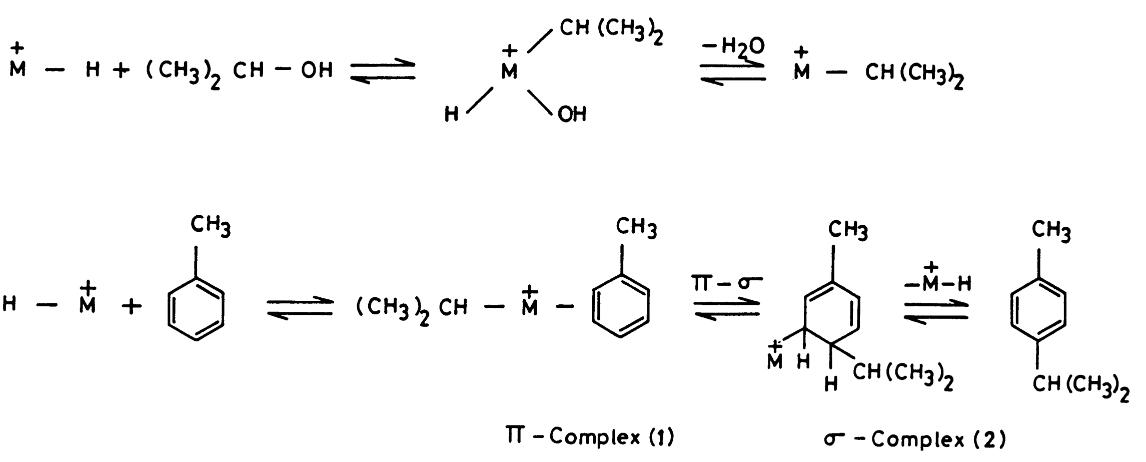
Fig. 3. Regeneration study over Tisial-5 catalyst. Reaction conditions; reaction temperature: 200 °C, LHSV: 0.5, 2-propanol/toluene (mole ratio)=1/3.

silica to alumina molar ratio of 16 (Tisial-4) appear to give optimum alkylation activity (Table 1 and Fig. 1). The comparison of the physicochemical characters as well as the activity for the alkylation of catalysts from Tisial-4 to Tisial-8 shows that the predominant factors governing the catalytic activity are the physical characteristics of the catalyst like surface area and pore volume, a higher value of which cause increased activity. However, the silica to alumina molar ratio also seems to be a controlling factor in the catalytic activity, which is evidenced by the lesser alkylating activity given by Tisial-2 and Tisial-3 with higher surface area and pore volume compared to Tisial-6 and Tisial-7 (Table 1 and Fig. 1).

The catalytic activity for the conversion of 2-propanol to alkylaromatics is much higher for Tisial-4 than for silica-alumina (Fig. 1). The surface area and pore volume for the latter are 135 $m^2 g^{-1}$ and 1.2 $cm^3 g^{-1}$ respectively and the corresponding values for Tisial-4 are 100 m^2 g^{-1} and 0.71 $cm^3 g^{-1}$ respectively. The silica to alumina molar ratio in both of these catalysts is 16. This reveals that the increased catalytic activity of Tisial-4 may be due to the presence of titania. When transition metal oxides are supported on silica-alumina, $\overset{+}{\mathrm{M}}\cdots\mathrm{H}$ species will be formed, where M is the transition metal.[28,29] These species initiate the alkylation reaction by the mechanism shown in Scheme 1.[28] The formation of the π-complex is possible because of the presence of low lying unoccupied d orbitals in the transition metal atom.[28,31] It may be presumed from the higher activity of the Tisial-4 catalyst that when titania is supported on silica-alumina, acid sites with suitable acid strength ($H_0 < +1.5$)[32] for the alkylation is increased. That is titania seems to exert a synergistic effect on silica-alumina.

Figure 1 also shows that the rate of formation of alkylaromatics remained constant with reaction time, for all the catalysts studied. In the product mixture the *p*-cymene content is more compared to *o*-cymene at a given time and the *o*-cymene concentration almost remained constant with reaction time. However, the rate of formation of *p*-cymene decreased with time and correspondingly the rate of formation of diisopropyltoluenes increased. This is illustrated in Fig. 2 by taking the case of Tisial-4. The trend of para-rich isomer may be due to the steric factors arising when the reacting species are adsorbed on adjoining sites.[33] Hence it can be assumed that the interaction between an adsorbed toluene molecule and the adsorbed alkylating moiety leads to the para isomer whereas the interaction of the latter with a free unadsorbed toluene in the gaseous state results in the ortho isomer. This also supports the observed lesser differences in the mol% of 2-propanol converted to *o*-cymene compared to that of *p*-cymene on Tisial-4, Tisial-5, and silica-alumina catalysts (Table 2). Also the simultaneous decrease of *p*-cymene and the increase of diisopropyltoluenes with time suggests that the *p*-cymene adsorbed is more prone to get further alkylated to produce diisopropyltoluenes. The results of the comparative study of Tisial-4 and silica-alumina show that the catalytic activity for the conversion of 2-propanol to alkylaromatics is increased by the presence of titania on silica-alumina.

Lesser amounts of alkyltoluenes are formed at temperatures lower than 200 °C. The optimum conversion of 2-propanol to alkylaromatics is observed at 200 °C (Table 3), above which it started decreasing. The increased conversion at 200 °C may be due to the effective diffusion of reactants into and the product molecules out from the pores of the catalyst.[34] The Lesser extent of formation of alkyltoluenes at temperatures 220 °C and 240 °C may be attributed to the possible formation of dealkylated product, namely toluene from the σ-complex (**2** of Scheme 1) by shifting the equilibrium. That is higher tempertures (>200 °C) favor the formation of toluene from the σ-complex, whereas lower temperatures give alkylated toluenes. This is inferred by the observation that the amount of unreacted toluene in the product mixture increased as the reaction temperature is increased



Scheme 1. The mechanism of alkylation catalyzed by transition metal oxide supported on silica-alumina.

beyond 200 °C (Table 4). Similarly, the dealkylation of formed cumene (isopropylbenzene) at temperatures >240 °C has also been observed by Baibuskii et al. over Y zeolite catalyst in the alkylation of benzene with propylene.[35]

In addition, the ortho isomer decreases marginally from 165 °C to 240 °C, while the para isomer shows an optimum at 200 °C (Table 3) and the ortho to para ratio decreases with increase of temperature. These observations are in line with those of alkylation reactions carried out on ion-exchanged zeolites.[32] Diisopropyltoluenes are formed in large amounts at lower temperatures (Table 3). This may be due to the high residence time of cymenes formed at lower temperatures resulting in further alkylation. In general, multialkylation may be favored at lower temperatures.[2]

Tisial-5 catalyst has been subjected to nine successive regenerations. The product pattern clearly indicate (Fig. 3) that alkylating activity of the catalyst is not appreciably affected by successive regenerations. This reveals that Tisial catalyst have sufficient active life for alkylation studies.

Conclusion

The silica-alumina supported titania catalysts are more active for the alkylation of toluene with 2-propanol than silica-alumina itself. Even in presence of titania, the physicochemical characteristics of the catalyst such as surface area, pore volume and silica to alumina molar ratio play a vital role in governing the catalytic activity. The Tisial catalyst co-precipitated from a solution of pH 4 has given the optimum conversion of 2-propanol to alkylaromatics. The para-rich isomer distribution can be attributed to steric factors. Multialkylation is found to be favoured at lower temperatures (<200 °C). The alkylating activity of the Tisial catalyst is not affected considerably by five successive regeneration cycles.

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References

1) H. Heinemann, *Catal. Rev.*, **8**, 312 (1974).

2) A. V. Deo, R. M. Cursetji, M. A. Purohit, V. G. Penkar, and V. V. Deshmukh, *Indian J. Technol.*, **21**, 363 (1983).

3) F. G. Devyer, P. J. Lewis, and F. H. Schineider, *Chem. Eng.*, **83**, 90 (1976).

4) E. F. Harper, D. Y. Ko, H. K. Lese, E. T. Sabourin, and R. C. Williamson, *ACS Symp. Ser.*, **55**, 371 (1977).

5) T. Saito, T. Tanno, Y. Iguchi, S. Shoji, (Hitachi Chem. Co., Ltd.) Ger. Offen. 2160465 (1972).

6) T. Saito, T. Tanno, T. Awano, and S. Shoji (Hitachi Ltd.) Ger. Offen 2239049 (1973).

7) C. C. Chiun (Mobil Oil Corp.) Eur. Patent Appl Ep 35836 16th Sep. 1981.

8) C. C. Chiun (mobil Oil Corp.) Eur. Patent Appl. Ep. 38116 21st Oct.1981.

9) C. C. Chiun (Mobil Oil Corp.) U. S. US 4302622 24th Nov.1981.

10) C. C. Chiun (Mobil Oil Corp.) U. S. US 4302620 24th Nov.1981.

11) K. Tarama, S. Yoshida, Y. Katayama, and T. Bitoh, *J. Jpn. Petroleum Inst.*, **11**, 771 (1968).

12) A. A. O. Kelly, *Ind. Eng. Chem.*, **39**, 154 (1947).

13) W. A. Schulze, U. S. Patent 2419796 April 29, 1947 to Phillips Petroleum.

14) E. F. Peter, U. S. Patent 2773108 Dec. 4,1956 to Standard Oil.

15) Y. Fukui, H. Takaoka, J. Ishii, and K. Hirai, *Bull. Chem. Soc. Jpn.*, **40**, 446 (1967).

16) Union carbide Bulletin F-2807(1966).

17) J. A. Rabo, U. S. Patent 3236721 Feb. 22, 1966 to Union Carbide.

18) R. N. Fleck, U. S. Patent 3298780 Jan. 17, 1967 to Union Oil Co.

19) J. J. Wise, U. S. Patent 3251897 May 17, 1966 to Socony Mobil Oil.

20) K. Tanabe, C. Ishiya, I. Matsuzaki, I. Ichikawa, and H. Hattori, *Bull. Chem. Soc. Jpn.*, **45**, 47 (1972).

21) Smith, W. Edward (General Electric Co.) Ger. Offen. 2716035 (1977).

22) I. Yusuke, H. Ress, and K. Vrabe, *J. Catal.*, **84**, 402 (1983).

23) V. G. Kumar, M. Rama Rao, P. V. Ravindran, and K. V. C. Rao, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2133 (1983).

24) V. G. Kumar, S. Venkatachalam, and K. V. C. Rao, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2317 (1984).

25) S. Venkatachalam, V. G. Kumar, and K. V. C. Rao, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 3805 (1984).

26) C. Groeneweld, P. P, M. M. Wittgen, H. R. M. Swinner, A. Wernsenn, and G. C. A. Schwitz, *J. Catal.*, **83**, 346 (1983).

27) I. M. Kolesnikov, L. M. Grinis, and Zh Prikl, *Khim (Leningrad)*, **55**, 340 (1982).

28) V. G. Kumar, T. S. Shoba, and K. V. C. Rao, *Tetrahedron Lett.*, **26**, 3281 (1985).

29) N. Calderon, J. P. Lawrence, and E. A. Ofstead, "Advances in Organometallic Chemistry," ed by F. G. A. Stone and R. West, Academic Press, New York (1977), p. 449

30) H. Werner and R. Feser, *Angew. Chem., Int. Ed. Engl.*, **18**, 157 (1979).

31) V. G. Kumar, T. S. Shoba, and K. V. C. Rao, *Tetrahedron Lett.*, **26**, 6245 (1985).

32) S. G. T. Bhat, *Indian J. Technol.*, **21**, 65 (1983).

33) S. G. T. Bhat, *J. Catal.*, **75**, 196 (1982).

34) T. Yashima, Y. Sakaguchi, and S. Namba, *Stud. Surf. Sci. Catal.*, **7**, 739 (1981).

35) V. L. Baibuskii, O. L. Knizhnikova, I. M. Gerzeliev, and S. N. Khadzhiev, *Khim. Tekhnol. Topl. Masel.*, **7**, 20 (1986).