Cyclodimerization of α-Methylstyrene under Homogeneous and Heterogeneous Acid Catalysis Conditions

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Received October 2, 2008

Abstract—The cyclodimerization of α -methylstyrene in the presence of Brönsted and Lewis acids was realized. The dependence of the cyclic α -methylstyrene dimer yield on the catalyst nature and structure was established. It was shown that the activity of the catalysts is determined by the strength of their acid sites, and the selectivity for the cyclic α -methylstyrene dimer depends on the nature of the anion (homogeneous acids) or the porous structure (heterogeneous catalysts). Sulfuric acid and silicophosphate exhibit the highest selectivity in the cyclodimerization of α -methylstyrene into 1,1,3-trimethyl-3-phenylindane.

DOI: 10.1134/S0965544109040082

According to [1], the dimerization of α -methylstyrene in the presence of acid catalysts, as a rule, leads to a mixture of 1,1,3-trimethyl-3-phenylindane (I), 4-methyl-2,4-diphenylpent-1-ene (II), 4-methyl-2,4-diphenylpent-2-ene (III), and α -methylstyrene trimers (IV):



As known from published data [1-5], the products and selectivity of the dimerization of α -methylstyrene depend on the catalyst nature and reaction conditions. The α -methylstyrene dimerization has been investigated in the presence of various homogeneous and heterogeneous acid catalysts, such as formic, phosphoric and chloroacetic acids, *p*-toluenesulfonic acid, cation exchangers, zinc, aluminum and titanium chlorides and phosphates, as well as zeolites. Cyclic dimer I is of considerable practical interest due to its high thermal and radiation stability. On the basis of I, lubricants, radiation-resistant coolants, jet fuels with a high heating value, and effective plasticizers for polymer materials can be obtained [6–8]. In this context, investigations aiming to develop highly selective catalysts for its synthesis are of current importance.

The present work is devoted to the investigation into the cyclodimerization of α -methylstyrene in the presence of acid catalysts of various natures and structures,



Fig. 1. Effect of (a) the amount of H_2SO_4 and (b) the temperature on the α -methylstyrene conversion and the selectivity for cyclic and linear dimerization products (130°C, 2 wt % of catalyst, 1 h): (1) α -methylstyrene conversion, (2) cyclic dimer, (3) linear dimers, and (4) trimers.

namely, Brönsted acids (sulfuric acid, cation exchangers, phosphomolybdic acid $H_3[P(Mo_2O_7)_6]$, and silicophosphate H_3PO_4/SiO_2 , ZnHPO₄) and aprotic Lewis acids (ZnCl₂, AlCl₃, Ti₂O₅ · P₂O₅).

EXPERIMENTAL

The α -methylstyrene cyclodimerization was carried out in a batch reactor at atmospheric pressure in the temperature range 50–140°C. Prior to use, α -methylstyrene was dried with calcined barium oxide and distilled under a vacuum; its purity was 99.8 wt %. The sulfuric acid used had a concentration of 93%. Phosphomolybdic acid of the analytical grade was dried at 150°C. The cation exchangers KU-2 and KU-23 (the 30/100 modification) were treated as described in [9] to have a static exchange capacity (SEC) of 5.3 (KU-2) and SEC = 4.9 (KU-23). Aluminum chloride was sublied in a vacuum. Zinc chloride was calcined at 200°C.

The product hydrocarbons were determined by GLC on a Tsvet chromatograph with a flame-ionization detector (2 m \times 2 mm metal column; stationary phase, 5% SE-30 on Chromaton HMDS; temperature programming from 50 to 280°C at a heating rate of 8°C/min; detector temperature, 250°C, evaporator temperature, 300°C) and a carrier gas (helium) flow rate of 30 ml/min.

RESULTS AND DISCUSSION

For the synthesis of the linear dimers of α -methylstyrene, 50–70% sulfuric acid is usually used. In our experiments, concentrated (93%) acid was used (Fig. 1).

As it can be seen, the quantity of the catalyst has a determining effect on the yield of **I**. In the presence of 0.1-1.0 wt % of sulfuric acid at $80-130^{\circ}$ C, a mixture of

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all dimers I-III is formed. As the amount of acid is increased to 2 wt %, I becomes the main product.

The amount of trimers does not increase, a fact that can be explained by the generation of a large number of carbocations, which interact with monomer molecules and thereby reduce the chain growth probability.

The investigation into the α -methylstyrene dimerization catalyzed by the cation exchangers KU-2 and KU-23 containing SO₃H groups on their surface showed that differences in the structure of the cationexchanger matrixes have a substantial influence on the composition of the reaction products (Figs. 2 and 3). For example, in the presence of the cation exchanger KU-2, the reaction proceeds with a high conversion of α -methylstyrene (94–98%); however, up to 90% of the linear dimers are formed.

By using the macroporous catalyst KU-23, under the selected conditions, cyclic dimer I is formed with a yield of 91–92 wt %. The higher catalytic activity of KU-23 in comparison with KU-2 can be explained by the absence of hindrances to the diffusion of α -methylstyrene molecules towards active sites inside catalyst grains. Note that the highest yield of I is achieved at 140°C, which is the limiting operating temperature of the cation exchanger; thus, its use is fraught with difficulties due to a short service life and a rapid loss of activity under these conditions.

It is known that heteropoly acids, for example, phosphomolybdic acid $H_3[P(Mo_2O_7)_6]$, display a higher activity and selectivity than mineral acids in many processes [10–11]. The calculated value for the strength of its proton centers is 1120–1130 kJ/mol, which is considerably higher than that of sulfuric acid (1170 kJ/mol) [12].

The study of α -methylstyrene dimerization in the presence of phosphomolybdic acid H₃[P(Mo₂O₇)₆] showed its high activity in the reaction; however, the



Fig. 2. Effect of (a) the amount of KU-2 and (b) the temperature on the α -methylstyrene conversion and the selectivity for cyclic and linear dimerization products (130°C, 2 wt % of catalyst, 2 h): (1) α -methylstyrene conversion, (2) cyclic dimer, (3) linear dimers, and (4) trimers.



Fig. 3. Effect of (a) the amount of KU-23 and (b) the temperature on the α -methylstyrene conversion and the selectivity for cyclic and linear dimerization products (130°C, 2 wt % of catalyst, 2 h): (1) α -methylstyrene conversion, (2) cyclic dimer, (3) linear dimers, and (4) trimers.

selectivity for **I** was lower than in the reaction with sulfuric acid (Fig. 4).

The maximum yield of I at 130°C in the presence of 5 wt % catalyst was 57 wt % over a reaction time of 1.5 h. In addition, the formation of considerable amounts of the α -methylstyrene trimers was observed in the presence of the heteropoly acid.

The results of the α -methylstyrene dimerization catalyzed by ZnCl₂, AlCl₃, and ZnHPO₄, as well as silicon and titanium oxides treated with phosphoric acid, are presented in the table.

It should be pointed out that the α -methylstyrene conversion in the presence of freshly sublimed aluminum chloride was very high and was increased by catalyst activation with HCl and water vapors. The results obtained demonstrate that the protonation of α -methylstyrene followed by its conversion into the carbonium ion necessarily involve proton centers. In the presence of aluminum or zinc chloride, a mixture of linear and cyclic dimers **I–III** was formed, of which **I** made up 40–70%.

We have found that silicophosphate, which is used for the hydration of ethylene into ethanol in industry, is a highly effective catalyst for α -methylstyrene cyclodimerization into **I**. The specific feature of this catalyst is that before its impregnation with phosphoric acid, the support (silica gel) is subjected to special hydrothermal treatment, as a result of which it acquires a microporous structure.

The average pore radius after the thermal treatment was 11 nm, which provided free access for monomer molecules to the catalyst active sites located inside the pores. On the silicophosphate surface, the terminal pro-

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Fig. 4. Dependence of the α -methylstyrene conversion and the selectivity for cyclic and linear dimerization products on the (a) HPA content and (b) temperature (130°C, 5 wt % of catalyst, 1 h): (1) α -methylstyrene conversion, (2) cyclic dimer, (3) linear dimers, and (4) trimers.

ton acid centers P-OH with PA = 1220 kJ/mol are present. There are no Lewis acid sites [13].

With the use of silicophosphate, the cyclodimerization of α -methylstyrene into I can be accomplished with a yield up to 94.7%, thus opening possibilities for the development of an efficient industrial process for the synthesis of practically important dimer I. Regarding fluorine-promoted silica, as well as zinc and titanium phosphates, all of these catalysts exhibit a high activity and selectivity in the synthesis of the linear dimers of α -methylstyrene.

As can be seen from the presented experimental results, phosphomolybdic and sulfuric acids, as well as silicophosphate, display the highest catalytic activity in

Catalyst	T, ℃	Reaction mixture composition					a-Methylstyrene	Selectivity
		α-methyl- styrene	α-dimer	β-dimer	cyclic dimer	trimers	conversion	for cyclic dimer, %
ZnCl ₂	50	16.8	40.2	27.5	15.1	0.4	83.2	18.1
	70	7.3	35.4	15.8	40.3	1.2	92.7	43.5
	90	1.3	20.5	10.7	65.2	1.7	98.1	66.5
AlCl ₃	50	15.4	39.7	26.0	18.3	0.6	84.6	21.6
	70	6.2	25.1	16.6	50.7	1.4	93.8	54.2
	90	1.5	15.7	10.5	70.4	1.9	98.5	71.5
$SiO_2 + 5\%$ F	50	40.7	40.8	16.6	1.8	0.1	59.3	3.0
	70	17.2	52.4	26.7	3.4	0.3	82.8	4.1
	90	4.5	55.7	33.6	5.8	0.4	95.5	6.1
ZnHPO ₄	50	12.3	62.4	23.6	1.7	-	87.7	1.9
	70	4.7	62.0	29.9	3.2	0.2	95.3	3.4
	90	2.9	61.4	30.5	4.9	0.3	97.1	5.1
$TiO_2 \cdot P_2O_5$	50	10.2	63.3	24.5	2.0	-	89.8	2.2
	70	3.5	61.7	31.5	3.1	0.2	96.5	3.2
	90	2.4	61.0	31.0	5.3	0.3	97.6	5.4
H ₃ PO ₄ /SiO ₂	50	14.3	54.7	27.4	3.6	-	85.7	4.2
	70	3.4	50.8	25.4	19.2	1.2	96.6	20.9
	90	2.5	2.9	0.9	92.3	1.4	97.5	94.7

The influence of the catalyst nature and temperature on the yield and composition of α -methylstyrene cyclodimerization products (5 wt % of catalyst, 6 h)

the cyclodimerization of α -methylstyrene into **I**. It should be noted that both the activity and selectivity of the tested homogeneous catalysts are substantially affected by the nature of the acid anion and those of the heterogeneous catalysts are determined by the size of the pores in which substrate molecules interact and from where the reaction products diffuse onto the outer surface.

Thus, it has been found that concentrated sulfuric acid and silicophosphate are the most active and selective catalysts for the cyclodimerization of α -methylstyrene into **I**. In the presence of 2–5 wt % silicophosphate at 90°C, the yield of **I** is 94.7 % with an α -methylstyrene conversion of 97.5–98%.

ACKNOWLEDGMENTS

This work was supported by the President of the Russian Foundation under the program of support of leading research schools, grant no. NSh-2349.2008.3.

REFERENCES

 Ya. I. Isakov, Kh. M. Minachev, V. Z. Sharf, et al., Neftekhimiya **39**, 278 (1999) [Pet. Chem. **39**, 251 (1999)].

- B. Chaudhuri and M. M. Sharma, Ind. Eng. Chem. Res. 28, 1755 (1989).
- M. Fujiwara, K. Kuraoka, T. Yarawa, et al., Chem. Commun., No. 16, 1523 (2000).
- G. N. Kirichenko, N. G. Grigor'eva, V. I. Glazunova, et al., in *Proceedings of 2 All-Russia Conference "Topical Problems of Petrolem Chemistry"*, Ufa, 2005, p. 78.
- N. G. Grigor'eva, E. A. Paukshtis, B. I. Kutepov, et al., Neftekhimiya 45, 453 (2005) [Pet. Chem. 45, 419 (2005)].
- 6. U. Ya. Margulis, *Radiation and Radiation Protection* (Atomizdat, Moscow, 1974) [in Russian].
- R. L. McLanghlin and J. W. Schick, US Patent No. 3,161,694 (1964).
- G. V. Leplyanin, S. R. Rafikov, G. N. Kirichenko, et al., USSR Inventor's Certificate No. 1 036 727, Byull. Izobret., No. 31 (1983).
- K. M. Saldadze, A. B. Pashkova, and V. S. Titov, in *Ion Exchange Resins*, Ed. by K. M. Saldadze (Gos. Nauchno-Tekh. Izd. Khim. Lit., Moscow, 1960).
- 10. I. V. Kozhevnikov, Usp. Khim. 62, 510 (1993).
- 11. M. Misono, Y. Konishi, and M. Furuta, Chem. Lett., No. 7, 709 (1978).
- 12. V. P. Shmachkova, N. S. Kotsarenko, and E. A. Paukshtis, Kinet. Katal. **45**, 587 (2004).
- 13. E. A. Paukshtis, *Infrared Spectroscopy in Heterogeneous* Acid Catalysis (Nauka, Novosibirsk, 1992) [in Russian].