ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 1065–1069. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.N. Khazipova, N.G. Grigor'eva, L.F. Korzhova, B.I. Kutepov, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 6, pp. 1008–1012.

MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Hydrogenation of α-Methylstyrene Linear Dimers in the Presence of Pd- and Ni-Containing Catalysts

A. N. Khazipova, N. G. Grigor'eva, L. F. Korzhova, and B. I. Kutepov

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, Ufa, Bashkortostan, Russia

Received December 11, 2008

Abstract—Hydrogenation of α-methylstyrene linear dimers and of 4-methyl-2,4-diphenylpentane on commercial Pd-containing and Ni (GM-3 grade) catalysts was studied under the following conditions: $T = 75–190°C$, $P(H_2) = 0.2–0.8$ MPa, $G_c = 2.5–10$ wt %, and $\tau = 1–4$ h.

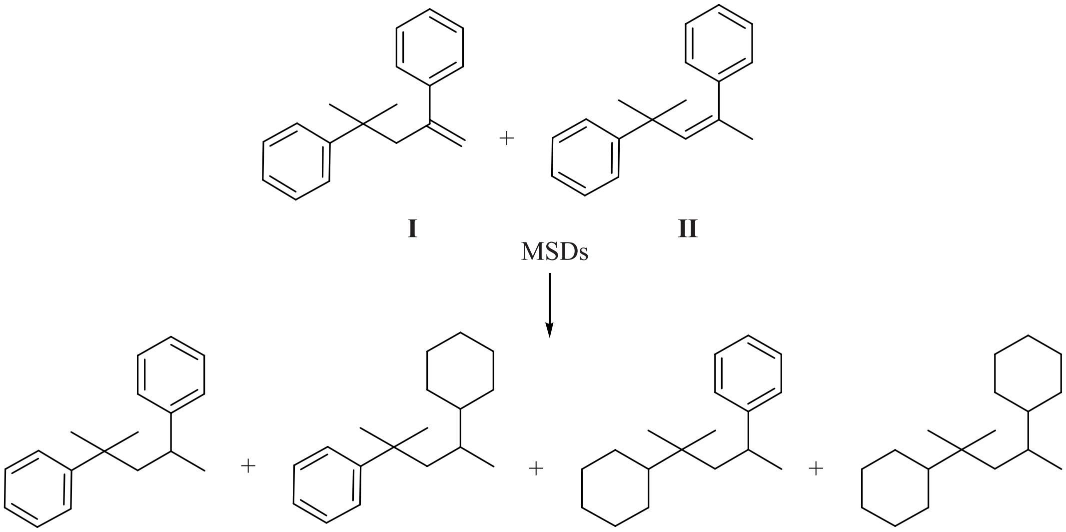
DOI: 10.1134/S1070427209060251

The development of synthetic oils receives much attention throughout the world. Possible raw materials for preparing high-quality synthetic oils are hydrogenated α-methylstyrene linear dimers (MSDs) **IV** and **V** (see scheme).

Oils containing 2-methyl-2,4-dicyclohexylpentane (**V**), compared to petroleum oils, ensure 1.2–2 times higher friction coefficient (0.09–0.1) and exhibit higher resistance to heat and oxidation. The Monsanto company (USA) developed and introduced into practice lubricating oils with unique properties based on mono- and dicyclohexylpentanes **IV** and **V** [1].

Procedures for preparing compounds **IV** and **V** have been described in numerous patents [2–5]. For hydrogenation of α-methylstyrene linear dimers **I** and **II**, it was suggested to use catalysts containing metallic Ni, Ru, Pd, or Pt. The reaction is performed at elevated pressure and a temperature from 70 to 200°C for 0.5–10 h.

It was interesting to examine the possibility of MSD hydrogenation at low pressure. Here we report on hydrogenation of MSDs and 4-methyl-2,4-diphenylpentane (**III**) (DPP) in the presence of commercial Pd- and Ni-containing catalysts at a pressure of 0.2–0.8 MPa.



Scheme of hydrogenation of α-methylstyrene linear dimers

EXPERIMENTAL

The following substances were taken as hydrogenation substrates: MSDs of the composition (wt %) 1,1,3-trimethyl-3-phenylindan (PI) 2.3, dimer **I** 92.2, and dimer **II** 5.5; product of MSD hydrogenation in hydrocarbon chain, 4-methyl-2,4-diphenylpentane (DPP, **III**), containing 99.8 wt % main substance.

MSDs were prepared by demerization of α-methylstyrene in the presence of HNaY zeolite (SiO_2/Al_2O_3 = 6.0, degree of decationization 0.52) by the procedure described in [6].

We studied commercial Pd-containing catalysts of AKG, PK-50, PKA-25-1, FPK-1, PKU-05, and MA-15 grades and GM-3 nickel catalyst. The catalyst particle size was 0.1–0.25 mm. Samples of Pd-containing catalysts were used both after preliminary activation in an H_2 stream at 100–300°C and without it. GM-3 nickel catalyst was preliminarily activated in an H_2 stream at 400–450°C.

The parameters of the pore structure of hydrogenation catalysts (volume and radius distribution of pores, specific surface area) were determined by low-temperature nitrogen adsorption with a Sorptomatik-1900 automated volumetric vacuum static installation (Fisons) [7–9] and by mercury porosimetry with a Porosimeter-2000 device [10].

Experiments on MSD and DPP hydrogenation were performed in an 80-ml isothermal pressure vessel. The ideal mixing mode was ensured by automatic vigorous shaking of the reactor. The starting mixture was loaded in an amount of 40 ml. It was prepared by dilution of the starting hydrocarbons (MSDs or DPP) with isooctane in 1 : 10 weight ratio. Hydrogenation was performed at T = 75–190°C, hydrogen pressure $P(H_2)$ = 0.2–0.8 MPa, and catalyst concentration G_c = 2.5–10 wt % for τ = 1–4 h.

The reaction products were analyzed chromatographically with a Carlo Erba HRGS 5300 Mega Series device equipped with a flame ionization detector and a capillary column coated with SE-30 phase. Analysis conditions: programmed heating from 50 to 280°C at a rate of 8 deg min^{-1}, detector temperature 250°C, vaporizer temperature 300°C, carrier gas helium, flow rate 30 ml min^{-1}. The reaction products were identified by GLC–MS on a Fisous Trio 1000 device. Analysis conditions: programmed heating from 50 to 320°C at a rate of 4 deg min^{-1}, T_{vap} = 260°C, carrier gas helium, flow rate 1 cm^3 s^{-1}, flow split ratio 1 : 100, MS source temperature 200°C, ionizing electrons energy 70 eV.

2-Methyl-2,4-diphenylpentane (DPP) (**III**). Mass spectrum, *m*/*z*: 238, 134, 120, 119, 105, 91, 77; Kovats index I_K = 1756.

2-Methyl-4-cyclohexyl-2-phenylpentane (MCHP) (**IVa**). Mass spectrum, *m*/*z*: 244, 134, 120, 119, 118, 91, 69; Kovats index I_K = 1794.

2-Methyl-2-cyclohexyl-4-phenylpentane (MCHP) (**IVb**). Mass spectrum, *m*/*z*: 244, 210, 160, 106, 105, 104, 83, 69; Kovats index I_K = 1791.

2-Methyl-2,4-dicyclohexylpentane (DCHP) (**V**). Mass spectrum, *m*/*z*: 250, 212, 187, 125, 111, 110, 97, 83, 69; Kovats index I_K = 1842.

The results of studying the physicochemical properties of commercial Pd-containing catalysts are

Table 1. Physicochemical properties of commercial Pd-containing catalysts

Catalyst	Pd content, wt %	Adsorption capacity for water vapor under static conditions, cm^3 g^{-1} (25°C, P/P_s = 0.5)	S_{sp}, m^2 g^{-1}, for nitrogen	V_{pore}, cm^3 g^{-1}	S_{sp}, m^2 g^{-1}	R_{av}, Å
				for mercury		
PK-50	0.5	0.07	164.0	0.72	183.0	62
PKA-25-1	0.25	0.07	236.0	0.67	182.5	50
MA-15	0.5	0.06	176.0	0.69	175.2	50
AKG	0.5	0.06	162.0	0.50	161.2	49
FPK-1	0.5	0.09	178.0	0.99	231.7	39
PKU-05	0.5	0.01	283.0	Not determined	Not determined	Not determined

given in Table 1. The characteristics of the Ni-containing catalyst are listed in Table 2.

It should be noted that only in PKU-05 catalyst the support is activated coal, and in the other catalysts the support is γ-Al_2O_3. The palladium content of the commercial catalysts varies from 0.25 to 0.5 wt %. The specific surface area of the commercial Pd-containing catalysts varies from 162.0 to 283.0 m^2 g^{-1}. Their total pore volume is 0.5–0.99 cm^3 g^{-1}. All the samples are characterized by a mesoporous structure. Pores with the radius from 40 to 100 Å make the major contribution to the total pore volume. Low adsorption capacity for water shows that the micropore volume is insignificant.

Preliminary experiments showed that MSDs and DPP did not undergo thermal transformations under the examined conditions. MSDs and DPP are also inert under the above-indicated conditions in the presence of γ-Al_2O_3 and SiO_2 (kieselguhr), which are supports of the catalysts under consideration. Replacement of nitrogen with hydrogen does not affect the results obtained. Hydrogenation of MSDs yields compounds with different degrees of hydrogenation (see scheme): DPP in which only the double bond in the hydrocarbon chain underwent hydrogenation, and also products of its partial (MCHP) and complete (DCHP) hydrogenation.

Table 2. Characteristics of the Ni-containing catalyst (GM-3 grade)

Parameter	Value
Nickel content, wt %	52.0
Sulfide sulfur content, wt %	0.3
Bulk weight, g cm^{-3}	0.5
Specific pore volume, cm^3 g^{-1}	0.6
Specific surface area, m^2 g^{-1}	280.0
Specific surface area of metallic Ni, m^2 g^{-1}	100.0

We found that the degree of MSD hydrogenation is determined by the nature of the catalyst (Fig. 1). The Pd-containing catalysts exhibit high activity and selectivity only in hydrogenation of the hydrocarbon chain of MSDs (Table 3). The reaction product in this case is DPP, and the selectivity of its formation is close to 100 wt % on virtually all the catalysts. The degree of conversion of MSDs to DPP on Pd-containing catalysts increases with time and reaches 99.2–100 wt % in 4 h. MA-15 catalyst is the least active. Further increase in temperature to 190°C does not appreciably affect the results of MSD hydrogenation.

Table 3. Conversion of α-methylstyrene dimers and selectivity of formation of particular products in the course of hydrogenation on Pd-containing catalysts. 150°C, hydrogen pressure 0.7 MPa, catalyst concentration 10 wt %, time 1–4 h; the same for Table 4

Sample	Time, h	Conversion, wt %	Formation selectivity, wt %		
			DPP	MCHP	DCHP
PK-50	1	41.4	100	–	–
	4	99.2	99.8	0.2	–
PKA-25-1	1	42.1	100	–	–
	4	96.5	100	–	–
MA-15	1	21.3	100	–	–
	4	47.6	98.3	1.7	–
AKG	1	40.9	100	–	–
	4	99.8	100	–	–
FPK-1	1	42.0	100	–	–
	4	99.6	100	–	–
PKU-05	1	42.8	100	–	–
	4	100	100	–	–

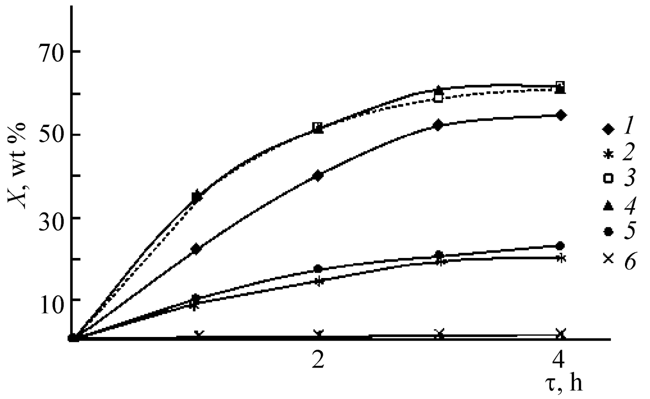


Fig. 1. Degree of MSDs conversion in isooctane X as a function of hydrogenation time τ. $T = 150°C$, $P(H_2) = 0.7$ MPa, $G_c = 10$ wt %. (*1*) AKG, (*2*) FPK-1, (*3*) PK-50, (*4*) PKU-05, (*5*) PKA-25-1, and (*6*) MA-15.

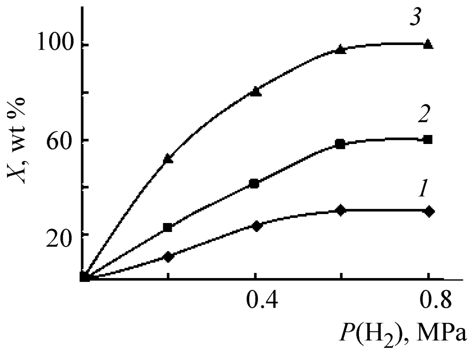


Fig. 2. Degree of MSDs conversion X on GM-3 catalyst as a function of hydrogen pressure $P(H_2)$. $G_c = 10$ wt %, $\tau = 4$ h. Hydrogenation temperature, °C: (*1*) 75, (*2*) 100, and (*3*) 150.

The results of DPP hydrogenation on various Pd-containing catalysts, given in Table 4, show that the catalysts differ in the hydrogenation activity.

The highest conversion of DPP is observed on AKG, PK-50, and PKU-05 catalysts: 54.2, 61.0, and 61.3 wt %, respectively. Thus, these catalysts are the most active among the examined Pd-containing catalysts, probably owing to larger surface area of the active metal.

Table 4. DPP conversion and selectivity of formation of particular products in the course of hydrogenation on Pd-containing catalysts

Sample	Time, h	Conversion, wt %	Formation selectivity, wt %	
			MCHP	DCHP
PK-50	1	34.0	96.2	3.8
	4	61.0	88.5	11.5
PKA-25-1	1	10.0	99.5	0.5
	4	22.6	96.9	3.1
MA-15	1	1.0	100	–
	4	1.0	100	–
AKG	1	22.0	97.3	2.7
	4	54.2	89.9	10.1
FPK-1	1	8.9	100	–
	4	19.7	96.8	3.2
PKU-05	1	34.6	95.9	4.1
	4	61.3	87.8	12.2

The major hydrogenation products of DPP are compounds with one cyclohexyl substituent (MCHP). The selectivity of their formation varies from 100 on low-activity samples (e.g., MA-15) to 87.8 wt % on the most active sample, PKU-05 (Table 4). The selectivity of formation of the exhaustive hydrogenation product, DCHP, does not exceed 12.2 wt % even on PKU-05 catalyst.

Prior to use, hydrogenation catalysts can be subjected to reductive treatment with hydrogen to enhance their activity. It is known [11] that an increase in the treatment temperature can lead to a change in the ratio of the atomic and hydride forms of hydrogen in the catalysts and, as a consequence, to changes in the catalytic activity. However, for the Pd-containing catalytic systems under consideration, an increase in the activation temperature from 100 to 300°C had no effect on the results obtained. Thus, under the examined conditions the commercial Pd-containing catalysts are highly active and selective only in hydrogenation of DPP to MSDs.

It is known [12, 13] that in hydrogenation of aromatic ring Ni-containing catalysts are more active than Pd catalysts. The results obtained in hydrogenation of MSDs on GM-3 catalyst (Fig. 2) show that virtually 100% conversion of the starting dimers was attained at 150°C. It should be noted that, in contrast to the Pd-containing catalysts, the major reaction product is DCHP. The selectivity of its formation is as high as 89.6 wt %. Also the hydrogenation products contain DPP and MCHP. The selectivity of their formation is 8.7 and 1.6 wt %, respectively.

In hydrogenation of DPP on GM-3 nickel catalyst, the results were similar: The DPP conversion was

Table 5. Influence of the concentration of GM-3 catalyst on the conversion and selectivity of formation of hydrogenation products. 150°C, hydrogen pressure 0.7 MPa, 4 h

Catalyst concentration, wt % relative to feed	Conversion, wt %	Formation selectivity, wt %		
		DPP	MCHP	DCHP
2.5	100	8.8	0.8	90.4
5.0	100	5.3	0.6	94.1
10.0	99.6	8.7	1.6	89.6

almost 100 wt %, and the selectivity of formation of the hydrogenation products, DCHP and MCHP, was 98.5 and 1.5 wt %, respectively.

We made an attempt to increase the selectivity of DCHP formation by increasing the hydrogenation temperature to 190°C. However, at 190°C, products of molecular weight lower than that of the starting dimers appeared: alkylbenzenes (ethylbenzene, isopropylbenzene, isobutylbenzenes), indan, methylindan, trimethylindan, alkylcyclohexanes. The results obtained show that the dimers undergo destructive transformations on acid centers present on the surface of GM-3 catalyst and described in [14]. Hence, the temperature of MSD and DPP hydrogenation should not exceed 150°C.

The results of studying the effect of the catalyst concentration in the reaction mixture on the MSD conversion and on the selectivity of formation of hydrogenation products are given in Table 5. It can be seen that, to convert MSDs to exhaustively hydrogenated DCHP, it is sufficient to take GM-3 catalyst in an amount of 2.5 wt % relative to feed.

To evaluate the stability of the catalytic properties of GM-3 catalyst at 150°C, $P(H_2) = 0.7$ MPa, and $G_c =$ 2.5 wt %, we performed ten successive experiments. No changes in the MSD conversion and in the selectivity with respect to particular products were observed.

CONCLUSIONS

(1) Hydrogenation of α-methylstyrene dimers in the presence of commercial palladium catalysts at a pressure less than 0.8 MPa yields 2-methyl-2,4-diphenylpentane with a high selectivity.

(2) Hydrogenation of α-methylstyrene dimers and 4-methyl-2,4-diphenylpentane to dicyclohexylpentane is possible on a nickel catalyst with the selectivity exceeding 95%.

REFERENCES

1. US Patent 3994816.
2. US Patent 6187979.
3. US Patent 6638417.
4. WO Patent 1778607.
5. US Patent 7015178.
6. Grigor'eva, N.G., Paukshtis, E.A., Kutepov, B.I., et al., *Neftekhimiya*, 2005, vol. 45, no. 6, p. 443.
7. Brunauer, S., *Adsorption of Gases and Vapors*, Princeton Univ. Press, 1943.
8. Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Area, and Porosity*, New York: Academic, 1982, 2nd ed.
9. Fenelonov, V.B., Okkel', L.G., Slyudkina, N.S., and Malygina, T.M., *Prib. Tekh. Eksp.*, 1997, no. 4, p. 133.
10. Plachenov, T.G. and Kolosentsev, S.D., *Porometriya* (Porosimetry), Leningrad: Khimiya, 1988.
11. Gan, T.O., Zh. Prikl. Khim., 1992, vol. 64, no. 8, p. 1804
12. Radchenko, E.D., Chesnokov, A.A., Pavlik, B.B., et al., *Povyshenie kachestva reaktivnykh topliv regulirovaniem ikh uglevodorodnogo sostava* (Improvement of the Quality of Propellants by Controlling Their Hydrocarbon Composition), Moscow: TsNIITEneftekhim, 1976.
13. Nogerbekov, B.Yu., Yablonskii, N.V., Dzharbolokova, N.U., and Dunaev, Yu.D., *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR*, 1976, no. 13.
14. Ione, K.G., *Nanesennye metallicheskie katalizatory prevrashcheniya uglevodorodov* (Supported Metal Catalysts for Hydrocarbon Transformations), Novosibirsk: Nauka, 1978, part 1.