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## CONVERSION OF n-BUTANE AND n-HEXANE ON ZIRCONIUM CONTAINING ZEOLITE CATALYSTS

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The conversion of n-butane and n-hexane on modified with  $\text{Pd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and sulfate - ions zirconium containing zeolite catalysts was studied. It was established that on the catalyst consisting of 10%  $\text{ZrO}_2$ , 4%  $\text{SO}_4^{2-}$ , 4% Co / HM<sub>[17]</sub> at a temperature of 190°C isobutane yield is 33.5 mol% for n-butane conversion of 47.6%, and on the catalyst, consisting of 5% Pd / HM<sub>[17]</sub> at 320°C isohexane yield is 73.5 mol% at a selectivity of 97.0%. The conversion of n-hexane at 150- 200°C accompanied by the formation of low and high molecular weight hydrocarbons with the yield of 3-6%. During such conversions the alkyl ions are formed, which interact with the other alkane ions and the resulting intermediates disproportionated to the hydrocarbons a smaller and a large number of carbon atoms as compared with the feedstock

**Key words:** *butane, hexane, isomerization, zirconium catalysts, sulfation, modifying mechanism, acid sites*

Modern, stricter requirements for motor fuels pose in front of the refining and petrochemical industry, the problem of creating gasoline production, components of which are high-octane unlimited satisfying environmental requirements alkanes branched structure [1-3]. Such components may be products of skeletal isomerization of n-alkanes. The process of isomerization of paraffinic hydrocarbons makes it possible to replace the environmentally undesirable aromatic hydrocarbons in gasoline by isocomponents - branched chain  $\text{C}_{5+}$  having the same high-octane properties. Compared with other ways of increasing the octane number of gasoline (alkylation, oxygenate, etc. additives), isomerizates characterized not only environmentally advantageously, but also a large availability of raw materials and lower cost.

Analysis of the development of isomerization processes and their current state shows the presence of technologies based on low, medium and high temperature catalysts. Literature on the isomerization of individual hydrocarbons  $\text{C}_4 - \text{C}_6$  summarized in [4, 5]. The main indicator responsible for the octane number of isomerizates is the temperature of a process of transformation of the starting materials. Carrying out the isomerization of n-alkanes at low temperatures facilitates obtaining more branched hydrocarbons. This requires a more active catalyst. Availa-

ble literature data suggest that the most promising for this purpose are nano-sized particles of zirconia. However, such catalyst systems do not investigated due to metastability of the catalytically active form of zirconia [6]. The latter publications dedicated to the above topics include papers presented at the Azeri-Russian symposium "Catalysis in solving the problems of petrochemical and refining" [7-9].

Improvement of existing technologies and the development of new catalysts with high activity and selectivity in the conversion of gasoline fractions is impossible without additional studies regularities of individual model isomerization reactions of alkanes. Therefore in the present work was investigated the conversion of n-butane and n-hexane on the modified zirconium containing zeolite catalysts.

## EXPERIMENTAL PART

The object of the study were the catalysts prepared by modifying with cobalt, palladium and / or zirconium the starting zeolite - a dealuminated mordenite with a modulus of 17 and HZSM-5 with a module of 64. For the preparation of the catalysts as the source of active components used salts of zirconium  $ZrO(NO_3)_2 \cdot 2H_2O$ , cobalt  $CoSO_4 \cdot 7H_2O$  and palladium  $[Pd(NH_3)_4]Cl_2$ . Modification of zeolites source depending on the purpose, conducted by dealkylation, dealumination, ion-impregnation introduction of various metals, impregnation sulphating agent solution ( $(NH_4)_2SO_4$  and  $H_2SO_4$ ) based on the number of  $SO_4^{2-}$  ions, and also by the method of solid phase modification. The method of solid phase modification was used for the one step preparation of sulfated zirconia-mordenite catalysts. For this purpose,  $NM_{17}$ ,  $ZrO(NO_3)_2 \cdot 2H_2O$ , and  $H_2SO_4$  are thoroughly mixed in a specific ratio and the resulting mass with a binder formatted into cylindrical "worms", and further dried at  $120^\circ C$  and calcined at  $350$  and  $550^\circ C$ . Sulfation of samples was performed as follows. Pre dealuminated mordenite was impregnated with a solution of a zirconium salt, and then dried at room temperature and calcined at  $550^\circ C$  for 5 hours. The resulting sample was impregnated with a given solution (based on the amount of  $SO_4^{2-}$  ions) of sulphating agent and formatted with a binder - alumina hydrogel taken based 25 g per 100 g dry weight of the catalyst. The formatted samples were dried at room temperature and then at  $110-120^\circ C$  for 3 hours and calcined at  $550^\circ C$  for 5 hours. Chemical composition of the synthesized catalysts is shown in Table 1.

**Table 1.** The chemical composition of the synthesized catalysts

Initial carrier	Active ingredient	Composition of the catalyst
HM(17)	Zr	5%Zr/ HM
	Co	5%Co/HM
	Pd	0.5% Pd /HM
	** Zr ,Co , SO <sub>4</sub>	10%Zr O <sub>2</sub> ,0.4%Co, 6%SO <sub>4</sub> <sup>2-</sup> / HM
	** Zr	HM <sub>17</sub> /10 % ZrO <sub>2</sub>
	Zr, Ni, SO <sub>4</sub>	10% Zr(OH) <sub>4</sub> ,0.5% Ni, 6%SO <sub>4</sub> <sup>2-</sup> /HM
HZSM-5		5% Zr /HZSM-5

\* All samples contain 25% Al<sub>2</sub>O<sub>3</sub>; \*\* Prepared by the method of solid phase modification

Feedstock served liquefied n-butane, pilot plant production VNIPIG az corresponding TU 51-946-80: n-butane - not less than 96.69 wt.%, isobutane-1.25 wt.%. n-hexane, brand ch.cl., containing composition 80.83 wt.% n-hexane.

Catalytic conversion of reactants on the synthesized samples was studied in a laboratory setting with a flow-type reactor. The volume of the catalyst loaded into the reactor, varied between 1-5sm<sup>3</sup>.

The isomerization of n-butane and n-hexane were studied at atmospheric pressure in the temperature range of 160-380<sup>0</sup>C, a molar ratio of H / CH = 3 and the feed volume velocity 2h<sup>-1</sup> (hexane), 150 h<sup>-1</sup> (butane) for the duration of experiments 1hour. Analysis of the reaction products was performed by GLC. Samples of the gas mixture leaving the reactor were taken with a syringe and were analyzed on a chromatograph of LXM 80 with a flame ionization detector on a column packed with carrier Chromosorb onto which loaded 10 wt.% Squalane (thermostating temperature of 70<sup>0</sup>C, pressure of the carrier gas - nitrogen - 0.8 - 0.9 kgc/cm<sup>2</sup>) and a length of 3 m with an inner diameter of 3 mm; and on a column filled with bricks of Inzen INZ-600 coated with apizon. In some cases, used chromatograph "AUTO System XL, Perkin Elmer», allowing to identify more precisely the hydrocarbon composition of gases, with a pre-created computer program.

## RESULTS AND DISCUSSION

### Catalytic properties of the testing specimens in the conversion of n-butane

The studies showed that, the n-butane is isomerized on the H-form of mordenite, yield of isobutane at 250<sup>0</sup>C to 20 min of reaction time reaches a maximum value (Table 1.) And then reduced to 60 min of reaction time up to 1.9%. Thus, except of the isobutane propane, n-and isopentanes are formed. The maximum yield of propane - the main reaction by-product, at the beginning of the reaction reaches 27% and within 60 min of reaction time reduced to 12%.

Yield of isopentane and n-pentane for 60 minutes remained at 2.0% and 1.0-1.5, respectively. Note that, when the temperature drops to 220<sup>0</sup>C propane yield decreases to a greater extent than the yield of isobutane, which leads to an increase in selectivity for the isomerization reaction and isopentane selectivity while substantially not given a sharp decrease in activity, changes little. These data will not be further considered.

Using as catalyst a dealuminated mordenite with a modulus of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> = 17, as can be seen from Table 2, can significantly improve the activity and selectivity for isomerization of n-butane. Therefore, further studies have used this form of mordenite (HM<sub>17</sub>).

**Table 2.** Conversion of n-butane on the modified forms of H-mordenite  
(V = 150 h<sup>-1</sup>, H<sub>2</sub>: n-C<sub>4</sub>H<sub>10</sub> = 2:1)

Catalyst	T, K	Composition of the contact gas, wt%. *					
		C <sub>1</sub> - C <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	i-C <sub>4</sub> H <sub>10</sub>	n-C <sub>4</sub> H <sub>10</sub>	i-C <sub>5</sub> H <sub>12</sub>	n-C <sub>5</sub> H <sub>12</sub>
HM	573	-	27.2	15.5	53.1	2.8	1.4
Co/HM	523	0.4	10.8	12.9	71.1	3.3	1.5
	573	0.5	34.8	16.3	44.8	2.6	1.0

\* - Data refer to the 20-min of the reaction

Introduction of the Co to the composition of HM as the dehydro-hydrogenating component enhances stability of the catalyst, without affecting the other catalytic parameters of the process. Given that in the conversion of normal alkanes the temperature reduction promotes increasing of the skeletal selectivity of isomeric components, further research has focused on the selection of catalyst systems based on HM<sub>17</sub>, allowing to reduce the temperature of the process.

Modification of the dealuminated HM<sub>17</sub> with the zirconium not only improves the yield of isobutane, but also reduce the temperature of the process (Table 3). If, on the source dealuminated mordenite conversion of n-butane at 220<sup>0</sup>C is 24.5%, and the yield of isobutane is 12.0%, the introduction of 10% ZrO<sub>2</sub> by solid phase modification, increases, compared with HM<sub>17</sub>, the conversion of butane about 2.2, and yield of isobutane 2.4 times (Table 3). Sulfation of HM<sub>17</sub>-ZrO<sub>2</sub> catalyst system contribute to the improvement of its isomerization properties.

**Table 3.** Isomerization of n-butane on a zirconium-containing mordenite catalysts prepared by solid-phase modification of HM<sub>17</sub>

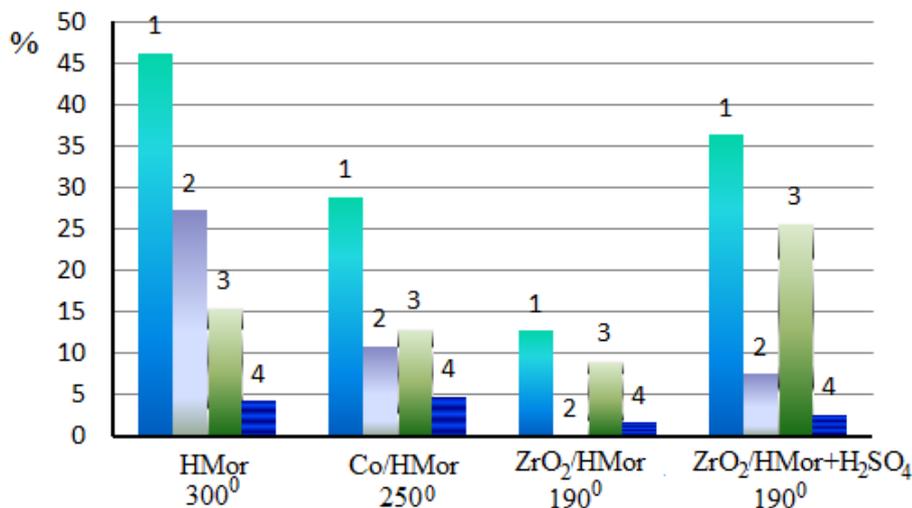
№	Catalysts	°C	Conversion of n-butane, %	Yield, wt. %.	
				isobutane	isopentane
1	HM <sub>10</sub>	250	34.8	12.8	2.0
2	HM <sub>17</sub>	220	24.5	12.0	0.6
3	HM <sub>17</sub> – 10 % ZrO <sub>2</sub>	190	12.7	9.1	1.6
		220	54.5	28.5	5.3

Table 4 shows the data of the isomerization of n-butane on sulfated zirconia catalysts prepared by solid phase modifying of the HM<sub>17</sub> with ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O salt.

**Table 4.** Conversion of n-butane on a sulfated zirconia-mordenite catalyst

Catalysts	°C	Conversion of n-butane, %	Yield, wt. %.		
			propane	isobutane	isopentane
[HM <sub>17</sub> + 10% ZrO <sub>2</sub> + 4% SO <sub>4</sub> <sup>2-</sup> ] (H <sub>2</sub> SO <sub>4</sub> )	190	36.4	7.5	25.7	2.6
	200	46.1	11.7	27.7	4.6
	220	50.3	14.5	30.0	4.9

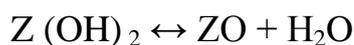
According to these data, the yields of isoparaffins for this type of catalysts at temperatures of 190-220<sup>0</sup>C are within 25.7-30.0% for n-butane conversion of 36.4-50.3%. The table shows that due to sulfation the catalyst acquires high activity and selectivity in the 190<sup>0</sup>C.

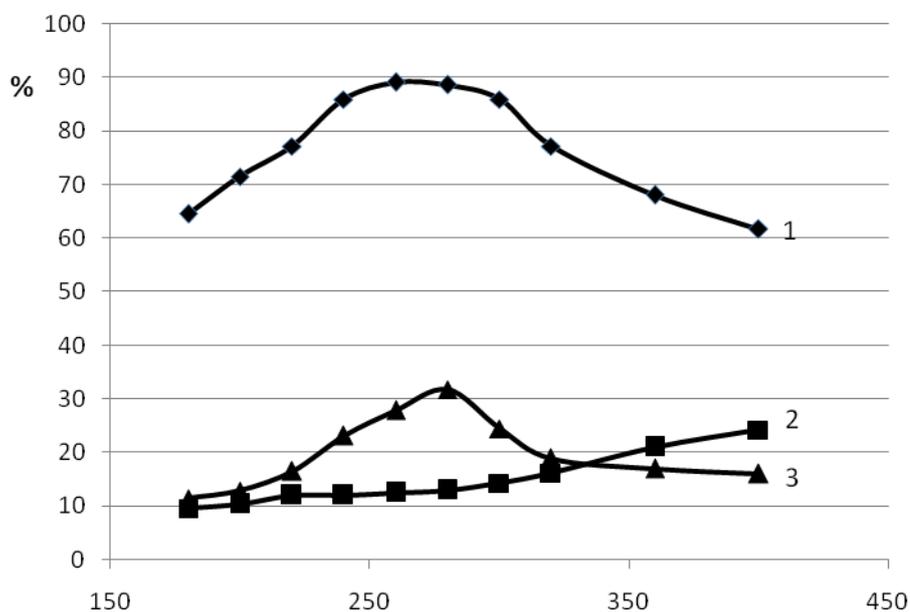


**Fig.1.** Conversion of n-butane on mordenite catalyst. 1-n-C<sub>4</sub>H<sub>10</sub> conversion; yield: 2 - C<sub>1</sub>-C<sub>3</sub> aliphatic hydrocarbons; 3 - izo-C<sub>4</sub>H<sub>10</sub>; 4 - C<sub>5</sub><sup>+</sup>

As can be seen from Fig. 1, with the modification not only changes the zeolite catalyst activity, but also is changed the distribution of reaction products of n-butane conversion, the change in properties of the zirconium catalyst systems due to the promotion of catalyst with sulfuric acid is explained by the transfer of catalyst in superacid state. Formation of pentane and propane is the result of bimolecular mutual influence of butane molecules, or in other words, the flow of the process to form a C<sub>8</sub> active derivatives, which formation are responsible the superacid centers [6, 10]. Indeed, the promotion of ZrO<sub>2</sub>/HM catalyst with sulfuric acid, i.e., transfer of catalyst to superacid state, leads to the selective formation of i-C<sub>4</sub>H<sub>10</sub> and significant increase in catalyst activity. However, it should be noted that the conversion of n-butane on Pd / HM<sub>17</sub> is also accompanied by the formation of C<sub>5</sub> alkanes. However, their formation is observed in a certain temperature range.

As can be seen from Figure 2. dependence of the yield of isopentane on the classic isomerization zeolite catalyst from the temperature is complex. If the temperature rise to 250<sup>0</sup>C is accompanied by a natural increase of the conversion, the subsequent increase in temperature reduces the activity the catalyst. This phenomenon can be explained by the decrease of density of Bronsted acid sites of the zeolite resulting from dehydration.





**Fig.2.** C<sub>4</sub>H<sub>10</sub> transformation on the catalyst Pd / HM and the effect of temperature on distribution of reaction products. 1 - the conversion of C<sub>4</sub>H<sub>10</sub>; Yield: 2 - CH<sub>4</sub>; 3 - C<sub>5+</sub>.

If the dehydration of zeolite in the range of 250<sup>0</sup>-300<sup>0</sup>C promotes release of pentane and isobutane, it can be assumed that the existing Bronsted centers acquire high acidity. The subsequent increase in temperature leads to a natural decrease in the concentration of these centers, and thus to a reduction in catalyst activity. Monotonic increase of methane with increasing temperature due to the increase of the centers ZO, possessing basic (nucleophilic) properties, may be a factor that confirms this assumption. Therefore, we can not exclude the formation of such centers on sulfated HM-ZrO<sub>2</sub> systems at relatively low temperatures.

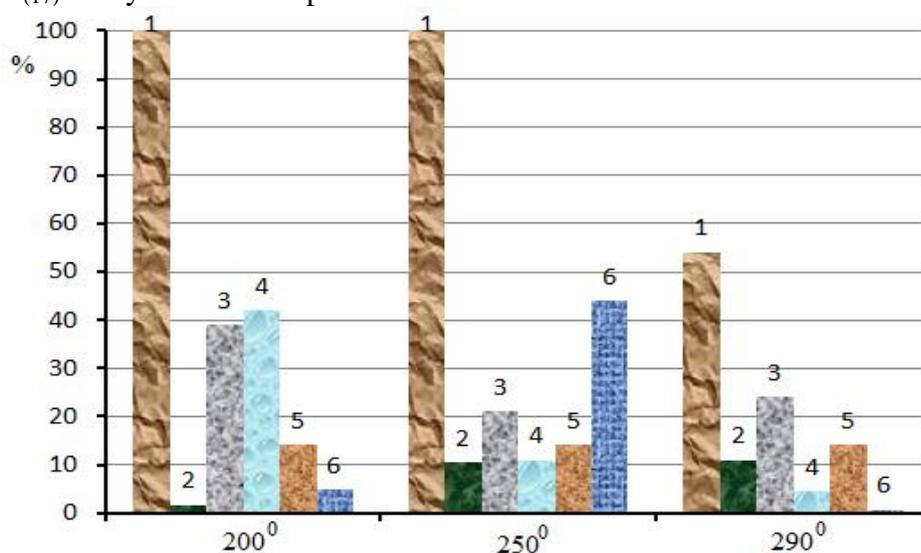
#### Catalytic properties of the testing specimens in the conversion of n-hexane

The flow of the process of isomerization of n-hexane depends from the catalyst and from the temperature. Use of the low temperatures reduces dehydrocyclisation and splitting of the reactant molecules, t.e. increases the selectivity of the process. However, in the temperature range of 250-340<sup>0</sup>C, mordenite catalyst, containing in its composition dehydro- hydrogenation components, exhibit high activity and selectivity in isomerisation of n-hexane. Table 5 shows the results of conversion of n-hexane at 0.5% Pd/NM17 catalyst. Total yield of isohexane (including 2,2-dimethylbutane - 18.3%) at a temperature of 320-340<sup>0</sup>C and volume velocity = 2h<sup>-1</sup> is 75.5-79%.

**Table 5.** The conversion of n-hexane over Pd / HM<sub>(17)</sub> catalyst (H<sub>2</sub>/C<sub>6</sub>H<sub>14</sub> = 3; v.v. = 2h<sup>-1</sup>).

Catalyst	T, K	Selectivity, %	Conversion of n-hexane, %
0.5%Pd/HM <sub>17</sub>	320	97.4	77.5
	340	95.5	82.7

Fig. 3 shows the temperature dependence of the conversion of n-hexane on not restored NiZrO<sub>2</sub>/HM<sub>(17)</sub> catalyst at low temperatures.



**Fig.3.** Dependence of conversion of n-hexane on the temperature over the unreduced NiZrO<sub>2</sub>/HM<sub>(17)</sub> catalyst. 1 – conversion of C<sub>6</sub>H<sub>14</sub>; Yield: 2 - C<sub>1</sub>-C<sub>3</sub>; 3 - C<sub>4</sub>; 4 - C<sub>5</sub>; 5 - i-C<sub>6</sub>; 6 - C<sub>7+</sub>.

From the results it is seen that at a temperature of 250<sup>0</sup>C and below the products of the conversion of n-hexane along with iso-C<sub>6</sub>, are also both low and high molecular hydrocarbons. Moreover, increasing the temperature from 200<sup>0</sup>C to 290<sup>0</sup>C at a practically complete conversion of n-hexane has a significant impact on the distribution of reaction products. At the same time, over the entire range of studied temperatures iso-hexanes yield remains constant and the yield of hydrocarbons C<sub>4</sub> and C<sub>5</sub> change more complex manner (Fig. 3). Increasing the temperature to 290<sup>0</sup>C leads to reduction in the overall activity of the catalyst. Here it is especially necessary to note that the value of C<sub>7+</sub> hydrocarbon's yield correlated with changes in the activity and decreases to 0, passing through a maximum at 250<sup>0</sup>C.

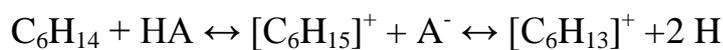
Increasing of the activity and selectivity on the isocomponent at temperatures above 250 K can be achieved on reduced Ni / HM catalyst. In this case the reaction is monomolecular and proceeds by a mechanism of formation of hexyl carbenium ions which is normal for the isomerization and the C<sub>7+</sub> hydrocarbons absent into the reaction products at elevated temperatures. Low activity of the unreduced catalyst at relatively high temperatures associated with the ionic

nature of the nickel present on the surface of the catalyst or, in other words, with the absence or reduction of its dehydrogenating function which is enhanced under the influence of  $ZrO_2$ .

It is known that by applying a platinum sulfated zirconia reduces isomerization temperature lower than  $100^{\circ}C$ , at a sufficiently high catalyst activity [6, 10]. A similar effect, as shown above sulfation has for  $ZrO_2$ - $NM_{17}$  in the isomerization of n-butane. Recovery of the  $SO_4^{2-}$  ions in the presence of hydrogen has a negative effect on the functioning of the catalyst. However, the higher reactivity of the n-hexane over n-butane on a sulfated  $ZrO_2$ - $NM_{17}$  catalyst promotes undesirable decay of this molecule to lower fragments. Introduction of the dehydrogenating components (Co, Ni) to the composition of zirconium mordenite contact, followed by reduction treatment at temperatures of  $450$ – $550^{\circ}C$  unlike unreduced, also had no positive effects on the isomerization activity of the corresponding catalyst.

Comparing the data obtained for the low temperature isomerization of n-butane and n-hexane, it is possible to make an assumption of a substantially different initial activation of these alkanes. Taking into account the possibility of the formation of the hexanon ions and probability of their formation dependence of the temperature, activity of the unreduced catalyst in conversion of n-hexane, as well as n-butane, can be explained by the predominance contribution of bimolecular mechanism which is associated with the superacide centers.

In this case, the formation of hydrocarbons having the number of atoms less or more than 6 in the molecule, involves the following activation step of  $n-C_6H_{14}$ :



at low temperatures leading to the formation and cleavage of  $[C_{12}H_{27}]^+$  on the unreduced catalyst.

Thus obtained results showed that on the catalyst consisting of 10%  $ZrO_2$ , 4%  $SO_4^{2-}$ , 0.4% Co /  $HM_{17}$  at a temperature of  $190^{\circ}C$  isobutane yield is 33.5 mol% for n-butane conversion of 47.6%, and on the catalyst, consisting of 5% Pd /  $HM_{17}$  at  $320^{\circ}C$  isohexane yield is 73.5 mol% at a selectivity of 97.0%. The conversion of n-hexane at  $150$ – $200^{\circ}C$  accompanied by the formation of low and high molecular weight hydrocarbons with the yield of 3–6%. During such conversions the alkyl ions are formed, which interact with the other alkane ions and the resulting intermediates disproportionated to the hydrocarbons a smaller and a large number of carbon atoms as compared with the feedstock.

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