

Description

The present invention relates to a novel method to produce Si/HZSM-5 catalyst and to use it in enhancing the output ratio of p-dimethylbenzene, p-diethylbenzene or p-ethyl-toluene through the alkylation or disproportionation of toluene and ethylbenzene.

This invention relates more specifically to the preparation of a novel Si/HZSM-5 catalyst through vapor phase deposition of Si on the surface of HZSM-5 catalyst which is obtained by ion exchanging ZSM-5 catalyst. The source of deposited Si comes from tetraalkyl ortho-silicate (or tetra-alkoxy silane), $\text{Si}(\text{OR})_4$, wherein R represents the alkyl group that contains 1-4 carbon atoms. The silicon deposit will substantially not clog the pores of the catalyst.

The purpose of the present invention is thus to make use of the modified catalyst in the alkylation or disproportionation reactions in order to enhance the yield of p-dialkylbenzene as an ingredient in the final product from aryl compounds such as toluene or ethylbenzene.

Dialkylbenzenes, including xylene, diethylbenzene and ethyltoluene, all have three sorts of isomers, namely p-, o- and m-dialkylbenzene. As to their industrial application, generally speaking, they can be used as organic solvent, resin bridging agent and can serve as a starting material for other specialized chemicals.

Generally speaking, p-dialkylbenzene has a broader spectrum of usage than their isomers. p-diethylbenzene can be directly used as the releasing agent in the course of separation of xylenes and therefore it is a chemical with potent high added value. The dehydrogenated product of p-methylstyrene can be polymerized, and the so-obtained polymer can in many respect displace the polystyrene, thus lessening the consumption of benzene and alleviating the shortage of benzene. Meanwhile, poly-p-methylstyrene uses directly the toluene as raw material, thus saving the consumption of hydrogen in the course of producing benzene from toluene through the process of hydrogenation and dealkylation and thus lowering the cost.

Dialkylbenzene can conventionally be synthesized by using the existing alkylation catalyst e.g. AlCl_3 -HCl and the unmodified ZSM-5. However, the conventional catalyst is void of selectivity to isomers. Therefore, the isomers of the aforesaid o-, m-, p-dialkylbenzenes can be resulted according to the ratio of thermodynamics. For instance, ethyltoluene is generated by the alkylation of ethylene and toluene. The equilibrium ratio in the thermodynamics is given as follows:

o-ethyl toluene : m-ethyltoluene : p-ethyl toluene = 16.3% : 49.9% : 33.7% (600° K)

As the boiling point of isomers closely approximates to one another, the relative volatility comes near 1. The separation is therefore difficult and the cost of operation is quite expensive. If AlCl_3 -HCl is used as the catalyst, not only separation is difficult but it is also impossible to avoid the loss of raw material due to multiple alkylation. Moreover, such a catalyst is liable to cause serious problems of pollution and corrosion due to its strong acidity.

The Mobil Petroleum Corporation of the United States developed, in 1972, a new type of catalyst, which is known as ZSM-5. The particulars of the method of production were disclosed as per U.S. Patent No. 3,702,886. The crystal structure of ZSM-5 catalyst has a specific order of arrangement and is a porous aluminum silicate crystal. The pores of this sort of catalyst has a homogeneous pore size and, therefore, some smaller than average particles are adsorbable and larger particles are repelled. Hence, it would be frequently referred to as "molecular sieve". There are many precedents in the industry in making use of this characteristic to conduct chemical reactions. The ZSM-5 catalyst is characterised by its selectivity, being able to satisfy the needs for high selectivity to product of different molecules, but its selectivity still falls short of expectations in respect of isomers of the same kind of product. For instance, when methyl alcohol and toluene are reacted over ZSM-5 catalyst, both the rate and the selectivity is very high for xylenes, but the ratio among the isomers of o-, m-, p-xylene remains near the equilibrium value in thermodynamics (refer to W.W. Kaeding, C. Chu, L.B. Yound, B. Weinstein, S.A. Butter, Journal of Catalysis, 67, p.159, 1981).

The ZSM-5 catalyst is a zeolite with high contents of silicon dioxide. Its silicon/aluminum ratio ranges from 20 to 10,000 or more. Its crystal system is $(\text{TPA})_2\text{O} - \text{Na}_2\text{O} - \text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$. In preparing this kind of catalyst the water solution containing tetra-propylammonium compound, sodium oxide, aluminum oxide, silicon oxide, is usually employed in a specific ratio, the composition is hermetically sealed for heating at 100°C to 175°C for a period of from six hours to 60 days to make possible the crystallization. The size of crystal particles, the ratio and specific characteristics of ingredients vary with the conditions of the reaction. The cation of the primitive catalyst such as TPA^+ , Na^+ and K^+ can be transferred into some other cations through the well-known techniques of ion exchange. The usually used substituents for cation are hydrogen ion, rare earth element ions, manganese ion and the ions of the Group II or VIII elements in the periodic table.

As commonly known in the art the modification of catalyst could be accomplished by means of

impregnation, poisoning of the active sites on external surface and steam treatment. Among these treatments, the impregnation process is most effective. The term "impregnation process" refers to the immersion of a ZSM-5 catalyst in a solution containing magnesium, phosphorus, boron or silicon-compounds and then air-dried and calcined to convert the compounds into oxides, thus obtaining a modified catalyst. Take, for example, the modification through the magnesium impregnation. The ammonium-contained $\text{NH}_4\text{ZSM-5}$ catalyst or hydrogen-contained HZSM-5 catalyst obtained after ion-exchanging is slurried in aqueous solution of magnesium acetate and is then heated at $70-95^\circ\text{C}$ and allowed to stand overnight. The viscous solution is placed in a crystalizing dish and dried in an oven at a relatively high temperature of about 120 to 200°C for about 10 hours. Finally it is calcined overnight at a temperature as high as about $500-550^\circ\text{C}$. As a result, the modified catalyst through immersion with adequate contents of magnesium is obtained. For phosphorous-modified catalyst, the solution of phosphoric acid, diammonium acid phosphate or trialkyl phosphine is used. The boiling point of such a solution is low. Therefore, the immersion is usually carried out at room temperature for a longer than average period of time, or otherwise, it may be distilled for a longer than average period of time with reflux column. Then, it is over dried slowly and calcined later on. However, the catalyst as modified through impregnation is reduced by far in activity and regenerability has demerits. Besides, during the synthesis of ZSM-5 catalyst, a slight difference in the operational conditions (such as the feeding of material, mixing of temperature, etc.) may oftenly result in significant difference in the performance of ZSM-5 catalyst, for each lot of the yield. Therefore, the modification of the catalyst through impregnation may oftenly make it impossible to render a judgment of the optimum amount of the modifier.

BRIEF DESCRIPTION OF THE DRAWINGS

- Fig. 1 Effect of different impregnating contents on reaction activity and selectivity to product
- Fig. 2 A comparison of activity between the magnesium-immersed catalyst and the catalyst modified by Si deposition during reaction
- Fig. 3 Effect of volume of $\text{Si}(\text{OC}_2\text{H}_5)_4$ added on Activity of alkylation and selectivity to product
- Fig. 4 A comparison of activity on different particle size of modified ZSM-5 catalyst

SUMMARY OF THE INVENTION

This invention is to modify ZSM-5 catalyst through the vapor phase deposition method so as to obtain a novel Si/HZSM-5 catalyst and, by making use of such a modified catalyst, the percentage of the content of p-dialkylbenzene may be enhanced in the yield of dialkylbenzenes.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENT

The novel Si/HZSM-5 catalyst under this invention is prepared by first ion-exchanging the catalyst ZSM-5 into catalyst HZSM-5, on to which is in turn deposited tetra alkyl orthosilicate by means of vapor phase deposition. More precisely the deposition process comprises the pulsating type vapor phase deposition during the reaction and the continuous type deposition during reaction.

According to the invention there is provided a process for the preparation of p-dialkylbenzene through the alkylation or disproportionation of mono-alkyl benzene using a HZSM-5 catalyst characterised by the fact that during the reaction there is deposited on the zeolite catalyst a sediment obtained through the vapor phase decomposition of a tetraalkyl orthosilicate of the formula $\text{Si}(\text{OR})_4$ wherein R represents an alkyl group containing 1-4 carbon atoms. The silicon deposit substantially will not clog the pores of the catalyst, as one of the features.

The present invention also uses the modified catalyst to promote the alkylation or disproportionation reactions of aryl compounds such as toluene or ethylbenzene so as to elevate the contents of p-dialkylbenzene in the yield of dialkylbenzenes.

The method under this invention is equally applicable to elevate the percentage of p-dialkylbenzene in the yield of dialkylbenzenes, either (1) in the case of xylene obtained through disproportionation of toluene, or obtained through the alkylation of methanol and toluene; or (2) in the case of diethylbenzene obtained through the disproportionation of ethylbenzene or otherwise obtained through the alkylation of a combination of ethylene, ethanol, and ethylbenzene; or (3) in the case of ethyltoluene as obtained through the alkylation of ethylene and toluene or that of ethanol and toluene. The reaction may proceed by contacting with Si/HZSM-5 catalyst at a temperature of from 200 to 500°C , a weight hourly space velocity of from 0.5 - 100 per hour (WHSV) and a pressure of from 0.006 to 0.89 MPa ($0-1000$ psig). The distribution of the reaction

products is mainly concentrated to the desired p-dialkylbenzene. Generally speaking, the size of the particles of the modified catalyst as used in the course of the reactions ranges from 0.01 to 30 μm and the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is larger than 20.

While ZSM-5 catalyst, as the precursor catalyst of Si/HZSM-5 catalyst, is processed through the well-known techniques, including, those steps as ion exchange, drying, calcination, etc., However, the present invention is to use the newly developed vapor phase deposition. This, in combination with the specialized physical properties inherent to ZSM-5 catalyst, can enhance the ratio of selectivity to product of p-dialkylbenzene, as a novel method that is highly effective. The following examples can best illustrate the process of this invention.

Example 1:

Modification of the conventional ZSM-5 catalyst by impregnation with magnesium:

The HZSM-5 after going through ion exchange is immersed in $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ solution of appropriate concentration for 24 hours and then is dried in a 100 °C oven. The catalyst is further calcined at 500 °C for 15 hours. In this manner, the impregnated compound is converted to oxide.

Example 2:

The reactivity of magnesium -impregnated catalyst :

Following the procedure given in Example 1 above, ZSM-5 catalyst with different contents of magnesium ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$) is used in the course of the reaction of ethylene and toluene. When the temperature of the reaction reaches 320 °C, the changing status of the conversion of ethylene and the selectivity of p-ethyltoluene along with the magnesium content is given in Fig. 1. As indicated in the figure, the ratio of selectivity to product of p-ethyltoluene is elevated rapidly in proportion to the increase in the contents of magnesium and then is leveled off. The conversion ratio of ethylene falls gradually with the increase in the magnesium contents.

Table 1

Magnesium-impregnated catalyst (Mg/HZSM-5) - Difference of reaction before and after regeneration		
conditions	before regeneration	after regeneration
Temperature (°C)	350	350
Pressure (MPa)	0.1013	0.1013 (0 psig)
Feed rate, Tol	12.8	12.8
(WHSV) C_2H_4	0.40	0.41
(Tol/ C_2H_4) mole	9.8	9.6
C_2H_4 conversion (%)	72.3	65.6
ET Selectivity (%)	81.1	83.2
ET yield (%)	58.7	54.6
p-ET (33.7)* (%)	72.5	66.8
m-ET (49.9)* (%)	27.3	33.0
o-ET (16.3)* (%)	0.2	0.2
time on stream (hrs)	16	14

* equilibrium fraction at 327 °C

Example 3:

New vapor phase deposition process for modifying HZSM-5 catalyst to Si/ZSH-5

----- (I) Pulsating type deposition before the reaction:

One gram of HZSM-5 catalyst, (crystal size about 3 μm and the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ about 90) is placed inside a reactor and retained in the reactor for 4 hours, with an air-borne saturated steam passing at a temperature of 540°C. The reactor is then purged with saturated steam to replace the air and is cooled to 320°C. The cooling process takes about two hours. The flow rates of the aforesaid air and nitrogen entrained steam are all 600 litres/kilogram catalyst/hour.

By pulsating injection at a temperature of 350°C with $\text{Si}(\text{OC}_2\text{H}_5)_4$ carried by nitrogen, 150 μl of $\text{Si}(\text{OC}_2\text{H}_5)_4$ is injected every two hours, until the predetermined amount has been fed. The ortho-silicate is decomposed and deposited as sediment of silicon, on the surface of the catalyst. The sediment, however, will not clog the pores of the catalyst, as a special feature.

Example 4:

New vapor phase deposition process for modifying HZSM-5 catalyst to Si/HZSM-5:

----- (II) Pulsating type deposition during the reaction:

Repeat the procedure of Example 3, except that the pulsating injection is effected at a temperature of 350°C. The feed of material is carried by the substantially high temperature gaseous substance under reaction. 150 μl of $\text{Si}(\text{OC}_2\text{H}_5)_4$ is injected every two hours, till the required volume is supplied. Silicide is deposited, after decomposition, as sediment of silicon on the surface of catalyst. The sediment, however, will not clog the pores of the catalyst, as a special feature.

Example 5:

The activity and regeneration of Si/HZSM-5 catalyst as modified by vapor phase pulsating injection method:

Table 2 is indicative of the deposition during reaction. This method is better than the deposition before reaction both in activity and selectivity to the desirable product. When compared with the previous immersion catalyst, it is understood that the catalyst as modified by the deposition of silicon is preferred in regeneration and better in activity. Especially, it is note-worthy that the selectivity to product of p-ethyltoluene in ethyltoluenes (ET) is as high as over 90%. This is the best result so far achieved through the modification of catalyst. Fig. 2 shows a comparison of activity between the magnesium-immersed catalyst in general and the catalyst modified by silicon in the deposition method.

Table 2: The Performance of the Catalyst
as Modified by Pulse Vapor Phase Silicon Deposition

conditions	unmodified HZSM-5 (90) II					deposition during reaction			
	1	2	3	4	After 1st regeneration	350	0,1013	16.7	after 2nd regeneration
Temperature (°C)	350	349	350	350	350	350	0,1013	16.7	350
Pressure (MPa)	0,1013	0,1013	0,1013	0,1013	0,1013	0,1013	0,1013	16.7	0,1013 (0. psig)
feed rate, Tol (WHSV) C ₂ H ₄	16.7	16.6	16.7	16.7	16.7	16.7	16.7	16.7	16.7
(Tol/C ₂ H ₄) mole	0.58	0.62	0.57	0.57	0.57	0.57	0.57	0.57	0.58
	8.8	8.1	8.9	8.9	8.9	8.9	8.9	8.9	8.8
C ₂ H ₄ conversion (%)	95.8	59.0	78.8	62.2	66.9	67.2	66.9	66.9	67.2
ET selectivity	77.0	86.5	83.1	84.1	83.8	83.7	83.8	83.8	83.7
ET yield (%)	73.8	51.0	65.5	52.3	56.1	56.2	56.1	56.1	56.2
p-ET (33.7) * (%)	29.3	92.5	98.3	99.6	99.4	99.4	99.4	99.4	99.4
m-ET (49.9) * (%)	63.7	7.5	1.3	0.4	0.6	0.6	0.6	0.6	0.6
o-ET (16.3) * (%)	7.0	0	0	0	0	0	0	0	0
time on stream (hrs)	16	20	29	45	12	17	12	12	17
accumulated amount of Si(OC ₂ H ₅) ₄ added (μl)	-	1050	1050	1900	1500	1500	1500	1500	1500

* equilibrium fraction at 327°C

Example 6:

Effect of Si(OC₂H₅) deposit amount upon reaction:

In accordance with the modification of catalyst as given in Example 4 under the same condition of

operation given in Example 5 various effects are observed with different amount of $\text{Si}(\text{OC}_2\text{H}_5)_4$ added. As indicated in Fig. 3, almost no o-ethyltoluene is produced in the course of the reaction. Therefore, a proper adjustment of volume of $\text{Si}(\text{OC}_2\text{H}_5)_4$ to be added may result in a different ratio of p-ethyltoluene/m-ethyltoluene. The dehydrogenated product may result in polymers of different physical properties after polymerization.

Example 7:

New vapor phase deposition process for modifying HZSM-5 catalyst to Si/HZSM-5 -- (III) continuous deposition during reaction:

Repeat the same procedure as in Example 3, except that 2% $\text{Si}(\text{OC}_2\text{H}_5)_4$ is used in the liquid starting material (toluene or ethylbenzene). Meantime the nitrogen with saturated steam at the same mole fraction is fed into the reactor. The conditions of the reaction should be kept at:

Pressure: 0, 1013 MPa (1 atmosphere)

Temperature: 320 °C

Feed ratio: 3.5 kg ethylbenzene/kg catalyst/hour

The product is analysed once every hour, until the fraction ratio of p-dialkylbenzene reaches 0.95, when the reaction is considered to be complete. The modification takes about 6 hours.

Example 8:

The reactivity of Si/HZSM-5 catalyst modified by continuous deposition during reaction disproportionation of ethylbenzene:

The catalyst obtained from Example 7 is used in contact with pure ethylbenzene as the feed. The reaction is to proceed under the following conditions of operations:

Pressure: 0, 1013 MPa (1 atmosphere)

Temperature at beginning of operation: 330 °C

Feed ratio: 3.5 kg ethylbenzene/kg catalyst/hour

Temperature at the end of operation: 400 °C

Average rise of temperature per day: 3.5 °C

Cycle of regeneration of catalyst: ~ 20 days

The following results may be obtained:

Conversion ratio: ~ 20%

Fraction ratio of p-diethylbenzene: 0.98

Benzene/diethylbenzene mole ratio: 1.4

Example 9

Effect of particle size of catalyst crystal upon its activity:

In case the particles are smaller than average (e.g. smaller than 1 μm), there will be more activated sites on the surface of the particles. As a result of being deposited on by silicon, the activity will greatly be reduced. Fig. 4 shows the relationship between the conversion and selectivity to product and volume of sediment of silicon in the course of the modification of ZSM-5 catalyst. As indicated in the Figure, the bigger the particles, the better the effect of modification.

Example 10:

Effect of catalyst binder:

The decomposition reactivity of $\text{Si}(\text{OC}_2\text{H}_5)_4$ varies with different bonding agent. The selection of proper bonding agent may result in a better reaction effect. Table 3 shows the temperature of decomposition of $\text{Si}(\text{OC}_2\text{H}_5)_4$ on different kinds of bonding material and HZSM-5 itself. Among those tested, Kieselguhr is the most inert one and, therefore, should be the best bonding material.

Table 3: A comparison of reactivity of $\text{Si}(\text{OEt})_4$
on different kinds of binder

	Temperature, °C
HZSM-5	< 180
$\text{SiO}_2\text{-Al}_2\text{O}_3$	< 180
$\gamma\text{-Al}_2\text{O}_3$	~ 230
Kieselguhr	> 320

$\text{Si}(\text{OEt})_4$ partial
pressure: 2000 Pa (15mmHg)

Time of Contact: 5 sec.

Conversion: 50%

Example 11

The catalyst is modified, under the following conditions of reaction,

Feed: Toluene: methanol: $\text{Si}(\text{OC}_4\text{H}_9)_4$ = 50:47:3 (percentage by volume), in combination with nitrogen and steam with same mole ratio.

Temperature: 180 °C

Pressure: 0,103 MPa (15 psia)

WHSV: 10 kg/kg catalyst/hour

Further in correspondence with Example 8, the catalyst which is modified according to the aforesaid method, is utilized to proceed disproportionation of ethylbenzene, under the following conditions of reaction:

Temperature: 320 °C

Pressure: 0,103 MPa (15 psia)

WHSV: 4.0 kg/kg catalyst/hour

The results of the reaction are given in Table 4

Table 4: Results of Reaction of Example 11

Duration Time for Modification of Catalyst (hour)	2	4	6	After Regeneration	
				Time on Stream (hour ¹)	4
Conversion (%)	19.08	14.83	8.33	9.55	8.42
Selectivity to Product (wt %)					
Diethylbenzene	58.54	50.53	49.27	51.13	54.09
Benzene	37.80	37.72	38.22	40.29	39.47
Diethylbenzene isomer (%)					
p-diethylbenzene	67.28	81.76	92.22	86.46	91.93
m-diethylbenzene	32.72	18.24	7.78	13.54	8.07
o-diethylbenzene	0	0	0	0	0

Example 12

The catalyst as modified according to Example 11 is utilized in the disproportionation of ethylbenzene, under various conditions, for 6 hours. The results of the reaction are given in Table 5.

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Table 5: Results of the reaction in Example 12

Conditions					
Temp. (°C)	320	360	360	360	400
Pressure (MPa)	1,82 (250 psig)	1,82	1,82	1,82	1,82
WHSV	3.95	3.95	8.41	17.34	17.34
Conversion (%)	20.46	35.23	18.0	8.55	12.96
Selectivity to product (wt%)					
Diethylbenzene	54.38	37.78	52.48	51.17	50.40
Benzene	37.33	44.54	38.91	38.42	39.57
Diethylbenzene isomer (%)					
p-diethylbenzene	66.36	58.46	78.41	85.65	75.21
m-diethylbenzene	31.03	36.64	20.68	14.35	22.31
o-diethylbenzene	2.61	1.90	0.91	0	2.48

Example 13

The catalyst, which is modified for 6 hours according to the method given in Example 11, is utilized to carry out the disproportionation of ethylbenzene under various conditions as stated in the following table. The results of the reaction are given in Table 6:

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Table : Results of reaction in Example

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RUN NO.	1	2	3	4
CONDITION OF REACTION				
TEMP. (°C)	320	360	360	360
PRESS. (MPa)	5,27	5,27	5,27	5,27 (750 psig)
WHSV	4.25	4.16	8.91	17.51
EB CONV. (%)	12.34	20.69	12.30	6.83
SELECTIVITY TO PROD. (WT%)				
B	38.12	39.86	41.34	38.85
DEB	53.98	45.83	51.02	55.57
ISOMER SELECTIVITY (%)				
P-DEB	77.83	70.60	80.36	85.15
M-DEB	20.67	28.11	19.64	14.85
O-DEB	1.49	1.29	0	0

Claims

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1. A process for the preparation of p-dialkylbenzene through the alkylation or disproportionation of mono-alkyl benzene using a HZSM-5 catalyst characterised by the fact that during the reaction there is deposited on the zeolite catalyst a sediment obtained through the vapor phase decomposition of a tetraalkyl orthosilicate of the formula $\text{Si}(\text{OR})_4$ wherein R represents an alkyl group containing 1-4 carbon atoms.
2. A process according to claim 1 wherein the reaction takes place in the presence of nitrogen and steam.
3. A process according to claim 1 characterised by the fact that the deposition is of the pulsating type.
4. A process according to claim 1 characterised by the fact that deposition is of the continuous type.
5. A process according to claims 1 to 4 wherein the di-alkyl benzene is p-dimethylbenzene, p-diethylbenzene or p-ethyltoluene.
6. A process according to claims 1 to 5 wherein the alkylation agents is ethylene, methanol or ethanol.
7. A process according to claims 1 to 5 wherein the reaction is carried out under the following conditions : temperature of 200 to 600 deg C; pressure of 0,205 to 7 MPa and WHSV of 0,5 to 100.
8. A process according to any of the preceding claims wherein the tetraalkyl orthosilicate is tetraethyl orthosilicate.

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Table : Results of reaction in Example 13

5	RUN No.	1	2	3	4
10	CONDITION OF REACTION				
	TEMP. (°C)	320	360	360	360
	PRESS. (MPa)	5,27	5,27	5,27	5,27 (750 psig)
15	WHSV	4.25	4.16	8.91	17.51
	EB CONV. (%)	12.34	20.69	12.30	6.83
	SELECTIVITY TO PROD. (WT%)				
20	B	38.12	39.86	41.34	38.85
	DEB	53.98	45.83	51.02	55.57
25	ISOMER SELECTIVITY (%)				
	P-DEB	77.83	70.60	80.36	85.15
	M-DEB	20.67	28.11	19.64	14.85
30	O-DEB	1.49	1.29	0	0

Claims

- 35 1. A process for the preparation of p-dialkylbenzene through the alkylation or disproportionation of mono-alkyl benzene using a HZSM-5 catalyst characterised by the fact that during the reaction there is deposited on the zeolite catalyst a sediment obtained through the vapor phase decomposition of a tetraalkyl orthosilicate of the formula $\text{Si}(\text{OR})_4$ wherein R represents an alkyl group containing 1-4 carbon atoms.
- 40 2. A process according to claim 1 wherein the reaction takes place in the presence of nitrogen and steam.
3. A process according to claim 1 characterised by the fact that the deposition is of the pulsating type.
- 45 4. A process according to claim 1 characterised by the fact that deposition is of the continuous type.
5. A process according to claims 1 to 4 wherein the di-alkyl benzene is p-dimethylbenzene, p-diethylbenzene or p-ethyltoluene.
- 50 6. A process according to claims 1 to 5 wherein the alkylation agents is ethylene, methanol or ethanol.
7. A process according to claims 1 to 5 wherein the reaction is carried out under the following conditions : temperature of 200 to 600 deg C; pressure of 0,205 to 7 MPa and WHSV of 0,5 to 100.
- 55 8. A process according to any of the preceding claims wherein the tetraalkyl orthosilicate is tetraethyl orthosilicate.



9. A process according to any of the preceding claims wherein there is used Kieselguhr as bonding agent for the catalyst.

Revendications

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1. Procédé pour la préparation de p-dialkylbenzène par alkylation ou disproportionnement de monoalkylbenzène en utilisant un catalyseur HZSM-5 caractérisé en ce que durant la réaction il est déposé sur le catalyseur un sédiment obtenu par la décomposition en phase gazeuse d'un orthosilicate de tétraalkyle de la formule $\text{Si}(\text{OR})_4$ dans laquelle R représente un groupe alkyle comprenant de 1 à 4 atomes de carbone.
2. Procédé selon la revendication 1 dans lequel la réaction a lieu en présence d'azote et de vapeur d'eau.
3. Procédé selon la revendication 1 caractérisé en ce que la déposition est du type pulsant.
4. Procédé selon la revendication 1 caractérisé en ce que la déposition est de type continu.
5. Procédé selon les revendications 1 à 4 dans lequel le dialkylbenzène est le p-diméthylbenzène, p-diéthylbenzène ou p-éthyltoluène.
6. Procédé selon les revendications 1 à 5 dans lequel l'agent d'alkylation est l'éthylène, le méthanol ou l'éthanol.
7. Procédé selon les revendications 1 à 5 dans lequel la réaction est menée dans les conditions suivantes : température de 200 à 600 °C; pression de 0,205 à 7 MPa et WHSV de 0,5 à 100.
8. Procédé selon n'importe laquelle des revendications précédentes dans lequel le tétraalkyl orthosilicate est le tétraéthyl orthosilicate.
9. Procédé selon n'importe laquelle des revendications précédentes dans lequel on utilise le Kieselguhr comme agent liant pour le catalyseur.

Patentansprüche

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1. Verfahren zur Herstellung von p-Dialkylbenzen durch Alkylierung oder Disproportionierung von Mono-Alkyl-Benzen mit einem HZSM-5 Katalysator, dadurch gekennzeichnet, dass ein durch Dampfphasenzersetzung eines Tetraalkylorthosilikats erhaltener Niederschlag sich während der Reaktion auf den zeolitischen Katalysator absetzt, wobei dieses Orthosilikat die Formel $\text{Si}(\text{OR})_4$ aufweist und R eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen darstellt.
2. Verfahren nach Anspruch 1, wobei die Reaktion in Anwesenheit von Stickstoff und Wasserdampf erfolgt.
3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Absetzung von pulsierender Art ist.
4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Absetzung von kontinuierlicher Art ist.
5. Verfahren nach Ansprüchen 1 bis 4, wobei das Dialkylbenzen p-Dimethylbenzen, p-Diethylbenzen oder p-Ethyltoluen ist.
6. Verfahren nach Ansprüchen 1 bis 5, wobei die Reaktion das Alkylierungsmittel Ethylen, Methanol oder Ethanol ist.
7. Verfahren nach Ansprüchen 1 bis 5, wobei die Reaktion unter den nachstehenden Verhältnissen ausgeführt wird: Temperatur von 200 bis 600 °C; Druck von 0,205 bis 7 MPa und WHSV von 0,5 bis 100.
8. Verfahren nach irgendwelchen der vorhergehenden Ansprüche, wobei das Tetraalkylorthosilikat Tetra-



ethylorthosilikat ist.

9. Verfahren nach irgendwelchen der vorhergehenden Ansprüche, wobei Kieselguhr als Bindemittel für den Katalysator benutzt wird.

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