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(57) Abstract

Catalyst system for selective alkylation of toluene with propylene. The catalyst system contains metallic sodium on a K_2CO_3 carrier and transition metal oxide, which advantageously is CeO_2, Dy_2O_3 or Fe_2O_3, as promotor. The invention also concerns a procedure for selective alkylation of toluene with propylene in the presence of a catalyst system.

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Catalyst system and procedure for selective alkylation of toluene

The invention concerns a catalyst system and procedure for selective alkylation of toluene.

There are two main methods to industrially produce alkylbenzene. One is Friedel-Crafts alkylation, which has the drawback that it tends to lead to polysubstitution (ring substitution) and, thereby, to difficult separation problems.

The other method uses base catalysts, such as Li, Na or K metals in the reaction between aromatic hydrocarbons and olefines. It is usual practice to use e.g. a K_2CO_3 carrier. An efficient side chain alkylating catalyst is obtained when metallic sodium is dispersed on the surface of dry potassium carbonate. An alkali metal catalyst produces a smaller number of different isomers than a Friedel-Crafts catalyst. The drawback is the comparatively low selectivity of the alkali metal catalyst to aromatics and its tendency to produce various isomers of alkylbenzene, which are hard to separate. Aliphatic dimers are also formed, although these are easily separated from alkylbenzene by distillation.

The selectivity of an alkyl metal catalyst is lowered at the preparation stage by oxygen and water residues in the K_2CO_3 carrier, whereby oxides and hydroxides are formed from part of the active metal. It is for this reason necessary to dry the carrier well at 120-150°C in vacuum for 10-20 hours and to prepare the catalyst in an inert atmosphere or in vacuum.

The x-ray diffraction spectrum run on unused catalyst reveals the presence of the following phases on the surface of the catalyst: Na_2O, K_2O, K_2CO_3, K, and only a minor quantity of metallic Na and liquid, amorphous Na/K alloy, although the diffraction from the latter cannot be observed. Thus the catalyst has to be prepared in

inert conditions in order to avoid oxidation. The alkali metal should be added in single doses as small as possible with the aid of a sodium press, or dispersed in an appropriate solvent; adequate dispersion is ensured in this way.

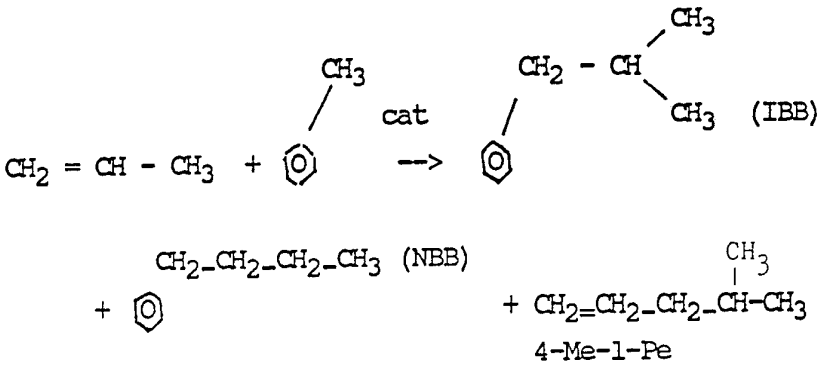
For improving the activity and selectivity of the Na/K_2CO_3 alkylation catalyst, various organic promotors may be used, such as butadiene, anthracene, graphite, heterocyclic nitrogen compounds (methylpyridines) and "acetylenic hydrocarbons", and oxygenous hydrocarbons. The effect of organic promotors has been said to be based on formation of a complex between metallic potassium and the promotor, and this complex would have higher activity than the alkali metal alone. The stability of such a complex in the reaction conditions applied (> 150°C) is however unlikely. Various, better results have been achieved using inorganic promotors: for instance metallic copper, cobalt, titanium and ground steel have been tried. It is clearly observable that promotors of various characters exert an effect on alkylation and dimerisation.

Catalysts like the catalyst of the invention are known in the art from other connections. As state of art is cited U.S. Patent No. 3,260,679, in which a catalyst system is disclosed which contains metallic sodium on an aluminium oxide carrier. As promotor for the metallic sodium serves a transition metal compound, advantageously an oxide. In the preparation of this catalyst, the sodium is added onto the aluminium oxide carrier, the carrier being first heated in a dry atmosphere to about 200-600oC. The sodium is added in fine powder form. The mixture is then agitated, whereby the sodium disperses on the surface of the aluminium oxide carrier. For transition metal oxide, in the reference iron oxide Fe_2O_3 is used. The impurities present in the catalyst have to be removed in order to attain sufficient life span of the catalyst. Use of these catalysts has been reported e.g. in conversion of 1-alkenes into 2-alkenes.

The object of the invention is a procedure by which the base catalyst used towards alkylating toluene with propylene is modified in

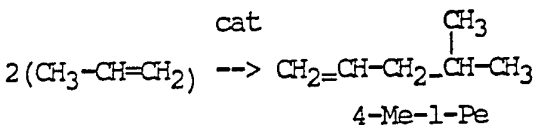
order to improve the activity, or yield, and selectivity of the catalyst. More specifically, the aims of the invention are:

to increase the proportion of the desired product IBB (isobutylbenzene) in the reaction



at the expense of the principal by-products 4-Me-1-Pe (4-methyl-1-pentene) and NBB (butylbenzene).

An influence can also be exerted on the dimerisation reaction



by modifying the catalyst of the invention and by using the correct amount thereof.

The catalyst system is mainly characterized in that it contains metallic sodium on a K_2CO_3 carrier, and a transition metal oxide as promotor.

The transition metal oxides used in the invention are advantageously cerium, dysprosium and iron oxide.

In the procedure of the invention the promotors increase the selectivity to isobutylbenzene or, on the other hand, to 4-methyl-1-

pentene and the activity of the catalyst. Promotors of the invention are transition metal oxides, advantageously CaO_2, Dy_2O_3 and Fe_2O_3.

The catalyst has for instance been prepared in a Schlenk glass vessel, in which case vacuum and nitrogen flushing may be used in aid. In this case only relatively small catalyst quantities at a time can be safely manufactured.

The problem has been how to provide efficient agitation in the glass system; and use of high enough temperature is necessary. The most efficient catalyst was obtained when the temperature was 200-250°C.

For this reason catalyst was also prepared in a steel mixer, in which at a time about 500 g of the catalyst could be manufactured, and which had efficient mechanical agitation.

The promotor is advantageously added to the catalyst at the reactor charging stage.

The alkylation reaction may be implemented as a charge, semi-charge or continuous process at temperature 100-200°C, preferably 140-160°C, and pressure 10-100 bar, preferably 40-70 bar. High pressure favours dimerisation of propylene. The proportion of olefine and aromate input may vary in the range from 10 to 0.5, preferably from 6 to 2. Higher ratios favour dimerisation of olefine, while lower ratios accelerate the quantity of alkylbenzenes. The semi-charge process is carried out under constant propylene pressure, and continuous propylene input to the reactor is provided. The reaction takes place in the aqueous phase. It is thus understood that the total pressure is constant and it is maintained with propylene.

The diffraction spectrum run on the catalyst shows that the sodium dispersed on the surface of K_2CO_3 is almost totally bound as Na_2O and as Na/K alloy and no presumed ion exchange K_2CO_3 to Na_2CO_3

takes place, at least not on the catalyst surface; the observed free K metal rather seems to originate in decomposition of carrier.

The following examples illustrate the procedure more closely.

Examples

With glass equipment, a basic catalyst was prepared, utilizing Schlenk technique. 50 g K_2CO_3 were weighed into a 250-ml Schlenk flask, kept in vacuum at about 230°C over night about 16 hrs and stored in a nitrogen chamber. Sodium pieces, washed with dry toluene, were weighed and added upon the potassium carbonate, in nitrogen atmosphere. Heating to about 200°C and dispersion of the molten sodium with the aid of a magnetic stirrer. In all trials sodium was added about 5% of the K_2CO_3 quantity.

Basic catalyst manufactured in a steel mixer was prepared 500 g at a time. Efficient mechanical agitation was provided in the vessel. Vacuum could not be used in this instance, but nitrogen flushing of the vessel could be arranged. All catalysts were immediately upon manufacturing transferred into a nitrogen chamber for storage and charging into the reactor. Sodium was used about 5% of the K_2CO_3 quantity. When the sodium was added to the carrier with the aid of a sodium press and continuous mixing was maintained at about 250°C, and a long reaction time was used, a catalyst was obtained which was highly efficient, but the catalyst formed a hard, compact cake, which was difficult to manage, owing to different metal proportion of the K/NA alloy. In reaction conditions, however, the catalyst is in molten state.

20 g of the catalyst were charged in a one-litre Parr reactor, in the nitrogen chamber. Thereafter, 213.11 g of water-free toluene and 115.18 g propylene were weighed into the reactor. The molar proportion of propylene and toluene was 1.19. Reaction temperature was 164°C and duration of test, 19 hrs. The pressure in the reactor was 43 bar at the beginning and 26 bar at the end.

In the examples, all promotors were added prior to charging the reactor with the catalyst.

The results are seen in Tables 1 and 2.

The tables reveal that, using the catalyst of the invention, one achieves better activity regarding IBB, or better IBB selectivity, compared with the reference examples. It should be noted that better yield automatically entails poorer selectivity. The tables also contain examples of how the promotor quantity affects the result.

Table 1

Catalysts prepared in metallic reactor

Run Code	Catalyst	Promotor	Promotor Quantity, [%]	IBB Select., [%]	4-Me-1-Pe Select., [%]	NBB Select., [%]	IBB Activity, [kg/kg cat]
1	A	CeO_2	5	72.77	5.67	8.71	6.47
2	A	Dy_2O_3	5	72.48	4.44	8.19	7.50
3	A	PbO_2, CeO_2	1.25 +1.25	73.16	6.81	8.19	5.61
4	A	Dy_2O_3, CeO_2	1.25 +1.25	74.68	4.01	8.32	6.37
5	A	CeO_2	1.25	72.96	5.42	8.34	6.45
6	A	Dy_2O_3	1.25	72.88	4.69	7.69	6.44
7 (Ref.)	B	MnO_2	2,5	73.69	5.79	8.11	5,26
8 (Ref.)	A	Naphthalene	2.5	72.69	5.43	7.37	4.64
9 (Ref.)	B	(Basic cat. II)		73.21	6.03	7.77	4.14
10 (Ref.)	B	TiO_2	2.5	73.12	5.14	7.91	4.91

Table 2

Catalysts prepared in glass reactor

Run Code	Cata-lyst	Promotor	Promotor Quantity, [%]	IBB Select., [%]	4-Me-1-Pe Select., [%]	NBB Select., [%]	IBB Activity, [kg/kg cat]
11	F	Fe_2O_3	2.5	76.03	5.60	7.78	4.86
12	K	B_2O_3	2.5	74.78	4.47	7.57	5.93
13	L	Dy_2O_3	2.5	70.24	4.63	7.22	6.24
15	F	Dy_2O_3	5.0	74.39	4.52	8.05	4.87
16 (Ref.)	J	Naphthalene + Toluene		72.13	5.65	7.54	4.41
17 (Ref.)	K	Basic catalyst Prop./Tol.=0.60		74.63	3.38	8.30	5.76
18 (Ref.)	K	(Basic cat.)		73.72	4.90	7.49	5.99

Claims

1. A catalyst system for selective alkylation of toluene with propylene, characterized in that it contains metallic sodium on a K_2CO_3 carrier and transition metal oxide as promotor.

2. Catalyst system according to claim 1, characterized in that the transition metal oxide used for promotor is a lantanide, advantageously CeO_2 or Dy_2O_3.

3. Catalyst system according to claim 1, characterized in that the transition metal oxide used for promotor is Fe_2O_3.

4. Catalyst system according to claim 1, 2 or 3, characterized in that the quantity of promotor is 1 to 5% of the catalyst quantity.

5. System according to any one of claims 1-4, characterized in that the quantity of sodium is 5% of the K_2CO_3 quantity.

6. A procedure for selective alkylation of toluene with propylene in the presence of a catalyst system, characterized in that the catalyst system consists of metallic sodium on a K_2CO_3 carrier and a transition metal oxide as promotor.

7. Procedure according to claim 6, characterized in that for promotor is used a transition metal oxide, advantageously CeO_2, Dy_2O_3 or Fe_2O_3.

8. Procedure according to claim 6 or 7, characterized in that the molar input proportion of olefine and aromatic is 10-0.5, preferably 6-2.

9. System according to any one of claims 6-8, characterized in that the promotor is added into the reactor at the charging stage.

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI87/00174

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC 4

B 01 J 23/04; C 07 C 3/52

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	B 01 J 23/04, /10, /76, /78; C 07 C 3/52
US Cl	252: 462, 474, 476; 502: 302, 303, 304, 327, 330, 344, 346, 355

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [8]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	GB, A, 1 269 280 (BP CHEMICALS LIMITED) 6 April 1972	
Y	EP, A3, 0 169 568 (PHILLIPS PETROLEUM COMPANY) 29 January 1986 & US, 4544790 JP, 61046248 US, 4609637	1
Y	US, A, 3 260 679 (T. M. O'GRADY et al) 12 July 1966	1, 3
Y	GB, A, 1 419 445 (SOCIETA' ITALIANA RESINE S.I.R.) 31 December 1975 & NL, 7312556 FR, 2200047 DE, 2347232 US, 3853786 CH, 578372 CA, 1002929	1

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IV. CERTIFICATION

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Swedish Patent Office	Britt-Marie Lundell

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