INFLUENCE OF CHROMIUM ENDOWMENT AND SURFACE AREA OF SILICA-ALUMINA CATALYSTS AND OF REACTION CONDITIONS ON BENZENE SYNTHESIS

PETER BECKER-HEIDMANN,¹ ACHIM HILLER² and JÖRG HOFMANN³

ABSTRACT. Radiocarbon laboratories using liquid scintillation counting depend on the availability of a catalyst for benzene synthesis. One of the two commonly used is a commercially available chromium-activated silica-alumina catalyst, PKN/D1. As this catalyst will no longer be produced, we have tested similar catalysts as possible replacements. We measured benzene purity by gas chromatography and mass spectrometry, and found that chromium endowment was crucial for a proper catalyst function. The surface area of the catalyst also significantly affected benzene yield and purity. We also studied the effects of different reaction conditions of acetylene absorption and benzene desorption on benzene purity. A catalyst with half of the Cr endowment and doubled specific surface area created yield and purity comparable to PKN/D1.

INTRODUCTION

A catalyst suitable for benzene synthesis in radiocarbon dating must produce benzene with 1) high yields to prevent isotope fractionation; and 2) high purity to prevent quenching in liquid scintillation counting. Noakes *et al.* (1965) studied several metal oxide alumina catalysts and found that all 5b, 6b and 7b group elements of the periodic table exhibited various degrees of ability to synthesize benzene. Whereas Noakes favored a vanadium-activated silica-alumina catalyst, V-0701 T 1/8" from Harshaw Chemical Co., Beechwood, Michigan with >90% yield and high purity, Pietig and Scharpenseel (1966) found the chromium-activated silica-alumina catalyst "Perlkatalysator PKN" produced by Solvay Catalysts GmbH, Hannover (formerly KaliChemie⁴) to produce benzene with high purity and yields of >90%. Both catalysts have been in worldwide use for radiocarbon dating since then. But both companies recently stopped the production of their catalysts, partly to avoid contamination of the environment, and partly because of the development of new catalysts. Our aim, therefore, was to find a substitute producing benzene with yield and purity comparable to the PKN/ D1 used in our laboratories.

MATERIAL AND METHODS

We tested four different silica-alumina catalysts offered by Solvay: 1) the commonly used PKN/D1, 2) PK200Tr, which is a preliminary stage in the production of PKN/D1 and differs in having half the Cr endowment and a doubled specific surface area, 3) PKN/D0, which is the same as PKN/D1 but without any Cr endowment, and 4) PKN/D9, which is a variety containing zeolites, with larger particle size but lower specific surface area (Table 1).

Using these catalysts we prepared benzene in the routine way in both Hamburg and Leipzig laboratories. Thereafter, we varied some of the conditions in order to optimize yield and purity of the produced benzene.

The standard reaction conditions of the Hamburg laboratory are: 1) 150 g fresh catalyst (we never re-use the catalyst) for 60–65 g SrCO₃, heated under vacuum at 300°C for 3 h to expel any water and contaminants before the reaction; 2) reaction temperature initially slightly increased to ca. 75°C,

²AG Paläoklimatologie, Universität Leipzig, Permoserstraße 15, D-04303 Leipzig, Germany

³Abteilung Hochtemperaturreaktionen, Institut für Technische Chemie, Universität Leipzig, Germany

⁴Now sold as "COM-Catalyst PKN/D1" by COMMERCIA Chemie GmbH, Am Uhrturm 16, 30519 Hannover, Germany

¹Institut für Bodenkunde, Universität Hamburg, Allende-Platz 2, D-20146 Hamburg, Germany

718 P. Becker-Heidmann, A. Hiller and J. Hofmann

of the Studied Cat	alyst Varieties	
Catalyst variety	Cr endowment (% of weight)	Specific surface area (m ² g ⁻¹)
PKN/D1	<i>ca</i> . 0.10	225 ± 25
PK200Tr	<i>ca</i> . 0.05	450 ± 50
PKN/D0	0	225 ± 25
PKN/D9	<i>ca</i> . 0.1	<i>ca</i> . 120

TABLE 1. Chromium Endowment and Specific Surface Area of the Studied Catalyst Varieties

after the end of the reaction, which lasts typically 1 h; 3) cautious pumping by section of remaining gases with benzene trap totally submerged in liquid nitrogen, then extraction with the catalyst heated to 160°C, and then to 200°C. At the Leipzig laboratory, normal conditions entail that the catalyst (~50-60 g for *ca.* 3 liter acetylene) is prepared for 4 h at 400-450°C in a muffle furnace. After evacuation of the catalyst container to *ca.* 1 Pa in 20 min, the acetylene is added to the catalyst while maintained at 0°C in an ice-water bath. The acetylene is added steadily until the reaction ceases in 15-20 min. After at least 1 h at 0°C, the benzene is extracted at a temperature up to 180°C for 10 min, and finally, a vacuum is applied for *ca.* 3 min.

All four catalyst varieties were used to prepare benzene under normal Hamburg laboratory conditions and also using the doubled amount of catalyst (300 g). Besides yield, the purity of the benzene was checked by gas chromatography (GC). The purity of the benzene produced under normal Leipzig laboratory conditions with PKN/D1 and PK200Tr was also analyzed by GC and additionally by mass spectrometry (MS) in a CH6 (Varian MAT[®]) mass spectrometer. The gas chromatograph was a Hewlett Packard[®] 5890 with a 25-m SE 54 (5% phenyl-modified polysilicone) column and hydrogen carrier gas. The temperature was set to 35°C for 10 min, then raised 20 K min⁻¹ to 200°C, where it was maintained for another 15 min.

For the following experiments we used only PKN/D1 and PK200Tr. In order to obtain more detailed information on the observed variations of yield and purity, we first analyzed the purity of several acetylene samples routinely synthesized from lithium carbide with a Chrompack[®] CP-9000 gas chromatograph using a 50-m-long 0.32-mm ID alumina/potassium chloride column and an FID detector. Then we chose the following approaches: 1) using purified tank acetylene for the trimerization step of the benzene synthesis (under normal Hamburg laboratory conditions), thus excluding all effects of by-products of the preceding acetylene synthesis; and 2) preparing benzene (under normal Leipzig laboratory conditions) with definite admixed portions of ethylene contamination to the tank acetylene. We used tank acetylene of grade 2.6 (Messer Griesheim, Lübeck, no. 1323) with guaranteed <0.4% contamination (mostly N₂ and O₂ and only traces of methane, ethane and ethylene), soluted in a matrix saturated with acetone. The acetone was kept in the tank by a slow transfer of the acetylene, and a cool trap at -50° C was set between tank and synthesis line. The volume of the synthesis line with a 6-liter container was calibrated and its temperature kept constant at 20°C. Based on the gauge pressure, the amount of acetylene was then calculated using the ideal gas equation of state, corrected by the compressibility factor for the established temperature.

We also improved the trace analysis by using combined GC/MS. Therefore, the HP 5890 was coupled to a Hewlett Packard[®] 5971A mass spectrometer. The Leipzig laboratory used a 12-m-long 0.2-mm ID SE 54 column and He carrier gas. After an initial isothermal period at 40°C, the temperature was raised by 8 K min⁻¹ to 200°C. The Hamburg laboratory used a 12-m-long 0.2-mm ID 0.33 μ m film HP-1 column and He carrier gas. The temperature was set to 40°C for 2.5 min, then increased at 5 K min⁻¹ to 270°C. Next, we varied some parameters of the benzene synthesis from the normal Leipzig laboratory conditions: The reaction time was decreased to 10 min and increased to 30 min from the normal *ca*. 20 min. The catalytic trimerization of the acetylene was conducted at room temperature and at 80– 90°C instead of at ice-water temperature. Then the benzene was extracted at 230°C, and within 1 h at 110°C instead of within 10 min at 180°C. Also, the vacuum application after the benzene extraction was omitted.

RESULTS AND DISCUSSION

Influence of Cr Endowment and Surface Area

A sample of the PKN/D0 catalyst, identical to the commonly used PKN/D1 but without Cr endowment, yielded only 33.8% benzene under Hamburg laboratory conditions, even though 300 g of the catalyst for *ca*. 5 g C were used. The purity of the benzene was only 96.9% measured by gas chromatography (Fig. 1). This means that the Cr endowment is essential for the catalytic reaction.



Fig. 1. Gas chromatogram of a sample prepared with PKN/D0 catalyst. All numbers are retention times. The peak at 3.16 min belongs to benzene. The peak at 2.22 min is 3.1%; the one at 2.33 min is 0.0082% of the benzene peak area in size. Neither compound was identified.

The PKN/D9, the variety with the same endowment as PKN/D1 but only *ca*. half the specific surface area because of an admixture of zeolites that also results in larger particles, yielded no benzene with the usual amount of 150 g and only 39.8% in total with 300 g of catalyst. From this, only 16.6% benzene was extractable, and the product had a strong acetone smell. We conclude that next to Cr endowment the specific surface area of the catalyst is crucial for yield and purity of benzene, and that silica-alumina is superior to zeolites.

PK200Tr differs from PKN/D1 in having a dimidiate Cr endowment and a doubled specific surface area. We found that the routinely performed benzene syntheses showed no significant differences between the old PKN/D1 and the PK200Tr catalyst. Also, both 150 g and 300 g of catalyst produced

720 P. Becker-Heidmann, A. Hiller and J. Hofmann

the same yield and purity of benzene, either with the original PKN/D1 or with PK200Tr. The purity of the benzene measured by GC was in each case >99.9%. The purity measured by MS of a series of 30 benzene samples prepared using PK200Tr and 10 benzene samples prepared with the PKN/D1 was generally >99.6%. The main trace components that we detected were toluene, ethylbenzene and naphthalene.

Influence of the Purity of Acetylene

The most critical step in the benzene synthesis procedure is acetylene synthesis. The purity of routinely produced acetylene measured on twelve samples varied between 96 and >99%. As did Witkin *et al.* (1993), we found ethylene (up to 3%) and ethane (up to 1%), and additional traces of butane, propene and propane (up to 0.15%) (*cf.* Table 4). We conducted some experiments under variable conditions of lithium carbide synthesis (temperature, addition rate of CO_2) and obtained similar results. Table 2 shows the GC/MS results of benzene yield and purity and Figure 2A-B shows two GC/MS chromatograms of the benzene synthesized from pure acetylene with PKN/D1 and PK200Tr. Pure ethylene reacted nearly quantitatively with PK200Tr catalyst, but <100-mg of liquid containing a wide variety of compounds in small amounts could be extracted.

cient cinom		lont	
0.	1 Cr	0.0	5 Cr
PKN/D1	PKN/D1	PKN200Tr	PKN200Tr
90.5	97.4	95.5	95.0
>99.99	>99.99	99.57	99.58
0.001	0.002	0.010	0.010
< 0.001	< 0.001	0.023	0.026
< 0.001	< 0.001	0.004	0.002
<0.001	< 0.001	0.002	0.001
< 0.001	< 0.001	0.001	0.001
< 0.001	0.001	0.003	0.002
	0 PKN/D1 90.5 >99.99 0.001 <0.001 <0.001 <0.001 <0.001 <0.001	0.1 Cr PKN/D1 PKN/D1 90.5 97.4 >99.99 >99.99 0.001 0.002 <0.001	0.1 Cr 0.0 PKN/D1 PKN/D1 PKN200Tr 90.5 97.4 95.5 >99.99 >99.99 99.57 0.001 0.002 0.010 <0.001

TABLE 2. Yield and Purity of Benzene Synthesized from Pure Tank Acetylene with Catalysts of Different Chromium Endowment



Fig. 2. GC/MS spectra of impurities of benzene produced from tank acetylene: A. with PKN/D1; B. with PK200Tr

Table 3 shows the results of two mixtures of acetylene and ethylene. The reaction stopped after a short time, when only 20–30% of the mixed gas had reacted. Only some 100 mg liquid could be extracted. Figure 3A-C shows GC/MS chromatograms of the benzene produced with acetylene of a normal sample and with the two artificial acetylene-ethylene mixtures. Besides the typical by-products, we found a variety of signals, presumably alkyl-substituted cyclopentanes and cyclohexanes. The clearly increased concentrations of ethylbenzene and cyclohexylbenzene (cf. Table 4) indicate that at least these two substances are probably formed by a coupled reaction between acetylene and ethylene at the surface of the catalyst.

TABLE 3. Purity of Benz lene Mixed with Differe	ene Synthesized f ent Amounts of Et	from Acety- hylene
Compound	26 Vol% ethylene	36 Vol% ethylene
Benzene	97.57%	97.49%
Toluene	356 ppm	390 ppm
Ethylbenzene	1.31%	1.00%
Isopropylbenzene	96 ppm	491 ppm
Isobutylbenzene	219 ppm	443 ppm
Naphthalene	277 ppm	347 ppm
Cyclohexylbenzene	6109 ppm	4931 ppm



Fig. 3. GC/MS spectra of impurities of benzene produced from: A. a normal sample; B. acetylene with 26% vol. ethylene; C. acetylene with 36% vol. ethylene

Variation of Reaction Conditions

Typical yields and GC/MS analyses of a larger set of experiments under varied conditions are compiled in Table 4. The total number of impurity compounds was *ca.* 30, but the most were present in amounts of only a few ppm. Due to the increased sensitivity of the GC/MS measurement, an additional number of trace compounds could be identified: xylene, isopropylbenzene (cumene), 1-methylpropylbenzene (isobutylbenzene), diethylbenzene, cyclohexylbenzene and biphenyl. Figure 4 is a typical gas chromatogram containing most of the by-products. The overall yield was constant at $87 \pm 2\%$, showing no influence of conditions nor of catalyst type.



Fig. 4. Typical gas chromatogram of synthesized benzene recorded with medium sensitivity and showing the most important impurities

Whether cooling during the catalytic reaction is performed by ice water or tap water seems to make no substantial difference in yield, purity or number of contaminants of the benzene. The greatest variety and often higher concentrations of impurities were produced when the reaction time was reduced. We found the least number of by-products in the samples extracted without the vacuum application step. In all samples, ethylbenzene was the main contaminant, followed by toluene, isobutylbenzene and naphthalene in varying order. In most cases, isobutylbenzene predominated compared to isopropylbenzene. Oxygen-containing contaminants such as acetone were of minor

BEN. Cyclice Envi. $m-f_{0}$ $e-xylene leopr. leopr. perrol. $	BEN. First. m-fr Solutions Ent.t. wayle	ents of Defizede synthesized with		Total				TRACE (OMPON	ENTS**		0						mana	C2C2.
ZENKE Actione Toluene bera: xylene bera: xylene bera: pylen tpan tpan<	TENE Acctone Tolence Tolence <thtolence< th=""> <thtolence< th=""> <thtol< td=""><td>It C₂H₆ number</td><td>number</td><td>number</td><td></td><td></td><th>BEN-</th><td></td><td></td><td>Ethyl-</td><td>-d/-m</td><td>o-xylene</td><td>Isopr</td><td>Isobu.</td><td>Diethyl</td><td>Naph-</td><td>Cyclo- hexvl-</td><td>Bi-</td><td>Ben-</td></thtol<></thtolence<></thtolence<>	It C ₂ H ₆ number	number	number			BEN-			Ethyl-	-d/-m	o-xylene	Isopr	Isobu.	Diethyl	Naph-	Cyclo- hexvl-	Bi-	Ben-
38 58 92 106 106 120 113 116 126 124	38 92 106 106 106 124 134 128 160 134 134 136 134 136 134 134 136 134 136	Ben- of <i>[%]</i> zene comp. vield <25	Ben- of zene comp. vield ~75	of comp. ~25		_	ZENE [%]	Acetone [ppm]	Toluene [ppm]	benz. [%]	xylene [<i>ppm</i>]	[mdd]	benz. [<i>ppm</i>]	benz. [<i>ppm</i>]	benz. [ppm]	thal. [<i>ppm</i>]	benz. [<i>ppm</i>]	phenyl [ppm]	zene conten
99.76 (11) 120 0.183 71 $n.d.$ 91 66 92.34 92.34 91.61 92.34 91.61 92.65 91.61 92.65 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61 92.61	99.76 (11) 120 0.183 7+ $n.d.$ 90 8 310 50 51 73 $n.d.$ 99.83 66 92.84 $n.d.$ 91.85 7 $n.d.$ 92.84 $n.d.$ 92.85 7 $n.d.$ 92.81 $n.d.$ 150 0.075 7 $n.d.$ 151 0.075 7 $n.d.$ 153 0.036 7 $n.d.$ 153 0.045 7 $n.d.$ 130 6.04 7 $n.d.$ 130 6.04 7 $n.d.$ 130 6.04 7 $n.d.$ 130 6.04 130 6.04 130 7 $n.d.$ 130 6.04 131 7 $n.d.$ 130 7 $n.d.$ 130 7 130	[%] ppm wt.:	[%] ppm wt.:	ppm wt.:	-IOM		78	58	92	106	106	106	120	134	134	128	160	154	(cm) [%]
99.84 nd 110 0.075 ? (9) 101 59 ca. 60 151 73 nd 99.34 (8) 280 0.436 ? (14) 86 316 26 129 101 99.34 (8) 280 0.436 ? (14) 86 316 26 129 nd 99.34 (7) (12) 0.012 (19) (14) 40 75 nd 139 33 42 99.34 (15) 207 0.106 (23) (17) 76 130 (21) 36 59 (19) 99.36 (14) 158 0.116 (23) (17) 76 130 211 37 30 51 (7) 99.36 (14) 158 0.164 105 74 211 136 131 76 30 99.36 (14) 158 174 113 76 131 <td< td=""><td>99.84 nd. 110 0075 7 (9) 101 59 α_{α} 131 0.035 7 (14) 36 135 135 0.04 99.44 99.44 (6) 130 0.045 7 (14) 36 135 135 0.04 130 0.045 7 n.d. 139 0.04 100 141 40 75 n.d. 119 33 42 99.48 (15) 237 0.047 7 n.d. 40 75 136 138 76 30 42 99.48 (17) 158 0.116 (23) (17) 76 130 201 71 33 42 99.48 (17) 158 0.116 (23) (17) 72 133 20 31 30 31 99.46 (13) 130 0.006 7 n.d. 42 30 42 99.47 (13) 1</td><td>0.11 87 9</td><td>87 9</td><td>6</td><td>_</td><td></td><th>99.76</th><td>(11)</td><td>120</td><td>0.183</td><td>71</td><td>t.d.t</td><td>40</td><td>211</td><td>n.d.</td><td>16</td><td>જ</td><td>n.d.</td><td>99.87</td></td<>	99.84 nd. 110 0075 7 (9) 101 59 α_{α} 131 0.035 7 (14) 36 135 135 0.04 99.44 99.44 (6) 130 0.045 7 (14) 36 135 135 0.04 130 0.045 7 n.d. 139 0.04 100 141 40 75 n.d. 119 33 42 99.48 (15) 237 0.047 7 n.d. 40 75 136 138 76 30 42 99.48 (17) 158 0.116 (23) (17) 76 130 201 71 33 42 99.48 (17) 158 0.116 (23) (17) 72 133 20 31 30 31 99.46 (13) 130 0.006 7 n.d. 42 30 42 99.47 (13) 1	0.11 87 9	87 9	6	_		99.76	(11)	120	0.183	71	t.d.t	40	211	n.d.	16	જ	n.d.	99.87
99.44 (8) 280 0.436 7 (14) 86 316 26 129 md. 139 93 42 93.94 (7) (12) 0012 (19) (10) (14) 40 7 $nd.$ 139 56 59 199 199 199 139 6047 7 $nd.$ 139 33 42 99.43 (15) 207 0.351 90 27 104 446 30 49 138 76 30 41 75 99.43 (15) 207 0.351 90 27 104 446 30 40 137 30 51 70 99.43 (17) 158 0.116 (23) (17) 76 130 217 104 44 30 37 399 37 399 37 399 37 399 37 399 37 399 37 399 37 399 37 <	99.44 (8) 280 0.436 7 (14) 86 316 26 126 129 nd. 139 99.44 (8) 280 0.436 7 nd. 136 156 169 33 42 99.48 (7) (12) 0.012 (19) (10) (14) 40 75 136 156 178 37 99.48 (15) 207 0.331 90 27 104 446 30 49 138 37 99.48 (17) 158 0.116 (23) (17) 76 130 (21) 30 61 (7) 99.46 nd. 174 nd. 76 130 (21) 30 61 (7) 99.47 nd. 144 30 21 21 21 21 21 21 21 21 21 21 21 21 21 21 21 21 2	86 9	86 9	6			99.84	n.d.	110	0.075	i	(6)	101	59	ca. 60	151	73	.p.u	
99.94 (7) (12) 0.012 (19) (10) (14) 40 (5) 36 59 (19) 99.48 (15) 207 0.331 90 27 104 46 30 49 138 33 42 99.48 (15) 207 0.331 90 27 104 46 30 49 138 33 37 99.48 (19) 233 0.064 105 n.d. 46 130 211 33 37 99.48 (19) 233 0.066 1 n.d. 45 174 n.d. 136 33 99.48 (10) 130 0.066 7 n.d. 45 174 n.d. 138 76 30 99.46 (10) 145 0.056 7 n.d. 31 39 119 36 17 39 37 399 37 99.46 101 130	99.94 (7) (12) 0.047 7 nd 119 33 42 99.48 (15) 207 0.31 90 27 104 446 30 49 33 42 99.48 (15) 207 0.351 90 27 104 446 30 49 138 37 99.48 (17) 158 0.116 (23) (17) 76 130 201 37 399 99.86 nd 130 0.066 7 nd 76 130 210 37 39997 99.87 nd 199 00071 7 nd 109 nd nd 9997 99.98 nd 199 0071 7 nd 109 nd 104 nd 104 104 104 104 104 104 104 104 104	89 13 87 11	87 11 87 11	11			99.44 99.82	(8) 19-11 19-11	280 150	0.436 0.096	c, c,	(14) n.d.	86 58	316 172	26 n.d.	126 136	129 163		
99.91 nd 131 0.047 7 nd 139 0.047 7 nd 119 33 42 33 42 33 42 33 42 33 42 33 42 33 42 33 42 33 42 33 42 33 42 33 42 33 42 33 43 33 42 33 42 33 42 33 43 33 43 33 33 61 (7) (7) 33 42 33 33 42 33 33 43 33 33 44 33 33 34 nd 33 33	99.91 n.d. 131 0.047 7 n.d. 119 33 42 99.48 (15) 207 0.351 90 27 104 446 30 49 198 53 99.48 (15) 207 0.351 90 27 104 446 30 49 198 53 99.48 (17) 158 0.116 (23) (17) 76 130 (21) 30 61 (7) 99.84 (19) 233 0.064 105 n.d. 45 174 n.d. 172 132 30 99.86 n.d. 199 0071 ? n.d. 31 30 134 n.d. 137 30 99.87 n.d. 199 0071 ? n.d. 313 40 136 76 30 99.81 n.d. 130 0066 ? n.d. 130 46 37 30 <td>86 5</td> <td>86 5</td> <td>5</td> <td></td> <td></td> <th>99.94</th> <td>Ē</td> <td>(12)</td> <td>0.012</td> <td>(19)</td> <td>(10)</td> <td>(14)</td> <td>6</td> <td><u>(</u></td> <td>36</td> <td>59</td> <td>(19)</td> <td></td>	86 5	86 5	5			99.94	Ē	(12)	0.012	(19)	(10)	(14)	6	<u>(</u>	36	59	(19)	
99.48 (15) 207 0.135 90 27 104 446 30 49 138 53 37 99.43 53 37 99.43 (15) 207 0.135 0.116 (22) 74 274 (21) 156 178 37 30 61 (7) 75 30 61 (7) 75 30 61 (7) 76 30 49 198 76 30 61 (7) 75 30 61 (7) 75 30 61 (7) 76 30 61 70 70 30 81 76 30 81 76 30 81 76 30 81 76 30 81 76 30 81 76 30 82 76 30 82 76 30 82 76 30 82 76 30 82 76 30 82 76 30 82 76 3	99.48 (15) 207 0.351 90 27 104 446 30 49 198 53 99.43 (8) 237 0.423 (16) (22) 74 274 (21) 156 178 37 99.43 (19) 233 0.064 105 nd. 61 75 30 61 (7) 99.84 (19) 233 0.064 105 nd. 45 174 nd. 18 76 30 99.86 nd. 130 0.066 ? nd. 34 nd. 118 76 30 99.97 nd. 139 0.071 ? nd. 33 103 nd. 104 30 37 30 99.97 nd. 139 0.073 ? nd. 33 103 nd. 104 46 37 39.94 99.97 0.073 ? nd. 103 103	ca. 10 min) 2 0.03 87 9	(1) 87 9	6			16.66	n.d.	131	0.047	۵.	n.d.	40	76	n.d.	611	33	42	
99.43 (8) 237 0.423 (16) (22) 74 274 (21) 156 178 37 30 61 77 30 51 77 30 51 77 30 51 77 30 51 77 30 51 77 30 51 77 30 50 51 75 30 51 76 30 51 76 30 51 76 30 51 76 30 30 51 76 30 51 76 30 <td>99.43 (8) 237 0.423 (15) (22) 74 274 (21) 156 178 37 97 97 99.43 (7) 158 0.116 (23) (17) 76 130 (21) 30 61 (7) 1 99.94 (19) 233 0.064 105 n.d. 45 174 n.d. 132 30 61 (7) (7) 133 0.066 7 n.d. 45 174 n.d. 172 132 30 99.97 99.96 n.d. 193 0.064 105 n.d. 31 30</td> <td>87 16</td> <td>87 16</td> <td>16</td> <td></td> <td></td> <th>99.48</th> <td>(15)</td> <td>207</td> <td>0.351</td> <td>90</td> <td>27</td> <td>104</td> <td>446</td> <td>30</td> <td>49</td> <td>198</td> <td>53</td> <td></td>	99.43 (8) 237 0.423 (15) (22) 74 274 (21) 156 178 37 97 97 99.43 (7) 158 0.116 (23) (17) 76 130 (21) 30 61 (7) 1 99.94 (19) 233 0.064 105 n.d. 45 174 n.d. 132 30 61 (7) (7) 133 0.066 7 n.d. 45 174 n.d. 172 132 30 99.97 99.96 n.d. 193 0.064 105 n.d. 31 30	87 16	87 16	16			99.48	(15)	207	0.351	90	27	104	446	30	49	198	53	
99.84 (19) 233 0.064 105 n.d. 45 174 n.d. 72 30 01 (1) 99.86 n.d. 130 0.066 ? n.d. 45 174 n.d. 72 132 35 99.86 n.d. 130 0.066 ? n.d. 45 174 n.d. 72 132 35 99.96 n.d. 199 0.071 ? n.d. 34 n.d. 123 34 n.d. n.d. 99.97 99.99 n.d. 199 0.071 ? n.d. 31 30 119 34 n.d. 133 34 n.d. 109 n.d. 104 n.d. 104	99.84 (19) 233 0.064 105 n.d. 45 174 n.d. 125 33 99.97 99.86 n.d. 130 0.066 ? n.d. 45 174 n.d. 76 30 99.86 n.d. 130 0.066 ? n.d. 45 174 n.d. 76 30 99.96 n.d. 199 0.071 ? n.d. 43 n.d. 112 76 30 99.97 (10) 195 0.071 ? n.d. 33 34 34 n.d. 103 n.d. m.d. 99.97 99.97 (10) 72 0.079 ? n.d. 31 50 (12) 44 29 (17) 99.91 n.d. 23 0.13 76 31 0.10 70 10 46 23 99.94 99.4 (3) 72 0.13 73 101 <th2< td=""><td>87 13 86 9</td><td>87 13 86 9</td><td>13 9</td><td></td><td></td><th>99.43 00 e0</th><td>® E</td><td>237 158</td><td>0.423</td><td>(16) (73)</td><td>(22)</td><td>74 76</td><td>274 130</td><td>(21)</td><td>156 30</td><td>178 61</td><td>37</td><td></td></th2<>	87 13 86 9	87 13 86 9	13 9			99.43 00 e0	® E	237 158	0.423	(16) (73)	(22)	74 76	274 130	(21)	156 30	178 61	37	
99.84 (19) 233 0.064 105 n.d. 45 174 n.d. 72 132 30 99.86 $n.d.$ 130 0.066 ? $n.d.$ 45 174 $n.d.$ 72 132 33 99.86 $n.d.$ 130 0.066 ? $n.d.$ 45 174 $n.d.$ 72 132 33 34 $n.d.$ 99.97 99.89 $n.d.$ 199 0.071 ? $n.d.$ 34 $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ 99.97 99.99 $n.d.$ 199 0.079 ? $n.d.$ 31 50 (12) 44 29 (17) 99.94 $n.d.$ 210 $n.d.$ 104 104 46 37 99.94 99.4 (10) 10.33 (11) 53 (13) 104 104 <t< td=""><td>99.84 $\left(19\right)$ 233 0.064 105 $n.d.$ 45 174 $n.d.$ 76 30 99.86 $n.d.$ 130 0.066 ? $n.d.$ 45 174 $n.d.$ 76 30 99.86 $n.d.$ 145 0.056 ? $n.d.$ 223 $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ 99.97 99.89 $n.d.$ 199 0.071 ? $n.d.$ 31 30 199 $n.d.$ 99.97 99.91 $n.d.$ 81 0.053 ? $n.d.$ 31 30 104 46 37 99.94 99.1 $n.d.$ 104 10</td><td>(up to ca. 30 min)</td><td>30 min)</td><td></td><td></td><td></td><th>00.00</th><td>E</td><td></td><td></td><td>Ì</td><td>(11)</td><td>2</td><td></td><td>(17)</td><td>R</td><td>5</td><td>S</td><td></td></t<>	99.84 $\left(19\right)$ 233 0.064 105 $n.d.$ 45 174 $n.d.$ 76 30 99.86 $n.d.$ 130 0.066 ? $n.d.$ 45 174 $n.d.$ 76 30 99.86 $n.d.$ 145 0.056 ? $n.d.$ 223 $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ 99.97 99.89 $n.d.$ 199 0.071 ? $n.d.$ 31 30 199 $n.d.$ 99.97 99.91 $n.d.$ 81 0.053 ? $n.d.$ 31 30 104 46 37 99.94 99.1 $n.d.$ 104 104 104 104 104 104 104 104 104 104 104 104 104 10	(up to ca. 30 min)	30 min)				00.00	E			Ì	(11)	2		(17)	R	5	S	
366 nd 145 0.026 ? nd nd (22) nd nd nd 99.97 389 nd 199 0.071 ? nd 34 34 nd 109 nd nd 99.97 389 (10) 195 0.071 ? nd 33 34 nd <	036 nd 145 0.026 ? nd nd (22) nd nd nd 99.97 036 nd 199 0.071 ? nd 34 nd	87 11 9 1.09 87 11 9 00 87 11 9	87 11 99	11 11	<u> </u>	<u>e</u> , s	9.84	(19) b n	233 130	0.064	105	D.d.	60 Å	152 174	.p.u	118 77	76	30 36	
96 $n.d$ 145 0.026 7 $n.d$ $n.d$ (22) $n.d$ $n.d$ $n.d$ 99.97 89 $n.d$ 199 0.071 ? $n.d$ 34 $n.d$ 109 $n.d$ $n.d$ 104 $n.d$ $n.d$ 101 $n.d$ $n.d$ 101 $n.d$ 101 $n.d$ 101 $n.d$ 101 $n.d$ 101 $n.d$ 101	96 $n.d.$ 145 0.026 7 $n.d.$ $n.d.$ (22) $n.d.$ $n.d.$ 99.97 89 $n.d.$ 199 0.071 ? $n.d.$ 34 $n.d.$ $n.d.$ 99.97 89 $n.d.$ 199 0.071 ? $n.d.$ 34 $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ $n.d.$ 99.94 109 (10) 195 0.073 ? $n.d.$ 30 0.13 0.14 0.14 0.14 0.14 0.14 104 46 37 99.94 111 96 157 0.143 ? $n.d.$ 110 44 29 (17) 0.16 286 0.079 ? $n.d.$ 110 44 29 (17) 99.94 0.16 1.6 1.10 439 $n.d.$ 104 $n.d.$ 104 104 104 104	after extraction omitted	action omitted	mitted		`	-) 				2			2	701	3	
89 n.d. 199 0.071 ? n.d. 34 34 n.d. 109 n.d. m.d. 90 (10) 195 0.047 ? n.d. 30 39 (19) 34 n.d. n.d. 90 (10) 195 0.047 ? n.d. 30 39 (19) 34 n.d. n.d. 91 $n.d.$ 81 0.053 ? $n.d.$ 30 95 $n.d.$ 104 46 37 99.94 71 96 157 0.143 ? n.d. 110 439 n.d. 101 247 n.d. 87 $n.d.$ 286 0.079 ? (11) 58 133 (13) 130 46 23 133 87 (4) (3) (3) (3) (3) (3) (3) (3) (3) (3) (3) (3) (3) (3)	39 n.d. 199 0.071 ? n.d. 34 34 n.d. 109 n.d. n.d. 30 (10) 195 0.047 ? n.d. 31 50 (12) 34 n.d. n.d. 30 (10) 195 0.047 ? n.d. 31 50 (12) 44 29 (17) 31 n.d. 81 0.053 ? n.d. 31 50 101 24 29 (17) 31 96 157 0.143 ? n.d. 110 439 n.d. 104 46 37 99.94 31 66 157 0.143 ? n.d. 110 244 104 46 23 34 n.d. 286 0.079 ? 110 43 103 46 23 351 61 131 55 133 130 46 13 130	7 0.03 86 4 99	86 4 99	4 99	66	8	.96	n.d.	145	0.026	۵.	п.d.	n.d.	(22)	n.d.	rd.	n.d.	n.d.	99.97
(10) 195 0.047 ? n.d. 30 39 (19) 34 n.d. n.d. (10) 195 0.047 ? n.d. 31 50 (12) 34 n.d. n.d. (11) 110 110 110 110 110 104 46 37 99.94 (11) 110 110 110 110 110 110 46 23 (21) 110 286 0.079 ? (11) 58 133 (13) 130 46 (23) eation step omitted 286 0.079 ? (11) 58 133 (13) 130 46 (23) (24) (5) 81 0.024 (5) (4) (14) (13) (2) (7) (1)	(10) 195 0.047 ? n.d. 30 39 (19) 34 n.d. n.d. (10) 195 0.047 ? n.d. 31 50 (12) 34 n.d. n.d. (11) 72 0.079 ? n.d. 31 50 (12) 44 29 (17) (11) 96 157 0.143 ? n.d. 110 439 n.d. 104 46 37 99.94 (12) 56 0.143 ? n.d. 110 439 n.d. 101 247 n.d. (31) 131 133 (13) 130 46 (23) 99.94 (4) (4) 31 55 (3) (13) (2) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) <td>89 7 99</td> <td>89 7 99</td> <td>- ²</td> <td>6</td> <td>S :</td> <th>.89</th> <td>n.d.</td> <td>199</td> <td>0.071</td> <td><i>.</i></td> <td>n.d.</td> <td>34</td> <td>34</td> <td>n.d.</td> <td>109</td> <td>n.d.</td> <td>n.d.</td> <td></td>	89 7 99	89 7 99	- ²	6	S :	.89	n.d.	199	0.071	<i>.</i>	n.d.	34	34	n.d.	109	n.d.	n.d.	
191 $n.d.$ 81 0.053 ? $n.d.$ 30 95 $n.d.$ 104 46 37 99.94 171 96 157 0.143 ? $n.d.$ 110 439 $n.d.$ 101 247 $n.d.$ 483 $n.d.$ 286 0.079 ? (11) 58 133 (13) 130 46 (23) cation step omitted 286 0.079 ? (11) 58 133 (13) 130 46 (23) cation step omitted (4) 39 0.083 (7) (8) (4) (2) (4) (2) (4) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (2) (3) (6) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1)<	01 $n.d.$ 81 0.053 $?$ $n.d.$ 30 95 $n.d.$ 104 46 37 99.94 71 96 157 0.143 ? $n.d.$ 110 439 $n.d.$ 101 247 $n.d.$ 83 $n.d.$ 286 0.079 ? (11) 58 133 (13) 130 46 (23) 81 0.083 (7) (8) 45 159 (9) (12) 52 (5) 94 (5) 81 0.024 (5) (4) (14) (13) (2) (7) (1) </td <td>80 80 80 80 80 80 80 80 80 80 80 80 80 8</td> <td>80 80 80 80 80 80 80</td> <td>~ ~ ~</td> <td>88</td> <td><u> </u></td> <th>8. 8.</th> <td><u>e</u>c</td> <td>21 27</td> <td>0.047 0.079</td> <td></td> <td>л. п.d.</td> <td>30 31</td> <td>8 33</td> <td>(61) (12)</td> <td>44 44</td> <td>n.d. 29</td> <td>n.d. (17)</td> <td></td>	80 80 80 80 80 80 80 80 80 80 80 80 80 8	80 80 80 80 80 80 80	~ ~ ~	88	<u> </u>	8. 8.	<u>e</u> c	21 27	0.047 0.079		л. п.d.	30 31	8 33	(61) (12)	44 44	n.d. 29	n.d. (17)	
171 $n.d.$ 81 0.033 7 $n.d.$ 30 95 $n.d.$ 104 46 37 99.94 171 96 157 0.143 ? $n.d.$ 110 439 $n.d.$ 101 247 $n.d.$ 483 $n.d.$ 286 0.079 ? (11) 58 133 (13) 130 46 23) cation step omitted 286 0.079 ? (11) 58 133 (13) 130 46 (23) sation step omitted (4) 39 0.083 (7) (8) 45 159 (9) (1) (1) (1) 94 (5) 81 0.024 (5) (4) (14) (13) (2) (7) (1) <td>17 $n.d.$ 81 0.033 7 $n.d.$ 30 95 $n.d.$ 104 46 37 99.94 171 96 157 0.143 7 n.d. 110 439 n.d. 101 247 n.d. 483 n.d. 286 0.079 ? (11) 58 133 (13) 130 46 (23) 481 0.143 ? n.d. 110 58 133 (13) 130 46 (23) 461 (1) 58 133 (13) 130 46 (23) 46 (5) 81 0.024 (5) (4) 31 55 (3) (8) (6) (1) 46 (5) 81 0.024 (5) (4) (14) (13) (2) (7) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1)</td> <td></td> <td>- - -</td> <td></td> <td>č</td> <td>2</td> <th></th> <td></td> <td>1</td> <td></td> <td>4</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	17 $n.d.$ 81 0.033 7 $n.d.$ 30 95 $n.d.$ 104 46 37 99.94 171 96 157 0.143 7 n.d. 110 439 n.d. 101 247 n.d. 483 n.d. 286 0.079 ? (11) 58 133 (13) 130 46 (23) 481 0.143 ? n.d. 110 58 133 (13) 130 46 (23) 461 (1) 58 133 (13) 130 46 (23) 46 (5) 81 0.024 (5) (4) 31 55 (3) (8) (6) (1) 46 (5) 81 0.024 (5) (4) (14) (13) (2) (7) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1)		- - -		č	2			1		4								
0.0 1.0 0.142 0.123 0.133 (11) 0.13 (12) 0.24 (2) (4) 0.123 (12) 0.22 (5) (6) (1)	0.0 1.0 0.14.5 0.13.5 <th0.5< th=""> <th0.5< th=""> <th0.5< <="" td=""><td>0 0.00 87 7 9</td><td>87 7 7</td><td></td><td>5` 8</td><td>5° 8</td><th>16.0</th><td>УЧ И</td><td>81</td><td>0.053</td><td>۰. د</td><td>יק ייק</td><td>30</td><td>95</td><td>n.d.</td><td>104</td><td>46</td><td>37</td><td>99.94</td></th0.5<></th0.5<></th0.5<>	0 0.00 87 7 9	87 7 7		5` 8	5° 8	16.0	УЧ И	81	0.053	۰. د	יק ייק	30	95	n.d.	104	46	37	99.94
cation step omitted 9.87 (4) 39 0.083 (7) (8) 45 159 (9) (12) 52 (5) 9.94 (5) 81 0.024 (5) (4) 31 55 (3) (8) (6) (1) 9.94 (4) (14) (13) (2) (7) (1) (1) (1) 9.94 (4) 159 0.188 (4) (4) (14) (13) (2) (7) (1) (1) 9.91 (10) 61 0.031 (4) (5) 36 106 (9) (8) (1)	cation step omitted 3.87 (4)390.083(7)(8)45159(9)(12)52(5) 9.94 (5)810.024(5)(4)3155(3)(8)(6)(1) 9.94 (4)1590.188(4)(4)(14)(13)(2)(7)(1)(1) 9.94 (4)1590.188(4)(4)(14)(13)(2)(7)(1)(1) 9.94 (4)161(0031(4)(5)36106(9)(8)(2)(1) 9.91 (10)610.031(4)(5)36106(9)(8)(1)(1) 9.94 (5)860.037(6)(3)(6)(8)(1)(3)(1)(1) 9.94 (5)860.037(6)(3)(6)(8)(1)(3)(1)(1) 9.94 (5)860.037(6)(3)(6)(8)(1)(2)(1) 9.94 (5)88(1)(6)(8)(1)(3)(2)(1) 9.94 (5)88(6)(6)(7)(6)(2589(2550 9.94 (5)88(6)(7)(6)(7)(6)(2589(2550 9.94 (5)88(6)(7)(6)(7)(6)(7)(7)(1) 9.94 </td <td>6 8 L8</td> <td>87 8</td> <td>1 00</td> <td>x 5.</td> <td>< .</td> <th>9.83</th> <td>n.d.</td> <td>286</td> <td>0.079</td> <td></td> <td>(11)</td> <td>58</td> <td>+33 133</td> <td>113) (13)</td> <td>130</td> <td>46 46</td> <td>п.u. (23)</td> <td></td>	6 8 L8	87 8	1 00	x 5.	< .	9.83	n.d.	286	0.079		(11)	58	+33 133	113) (13)	130	46 46	п.u. (23)	
9.87 (4) 39 0.083 (7) (8) 45 159 (9) (12) 52 (5) 9.94 (5) 81 0.024 (5) (4) 31 55 (3) (8) (6) (1) 9.94 (4) 159 0.188 (4) (14) (13) (2) (7) (1) <	9.87 (4) 39 0.083 (7) (8) 45 159 (9) (12) 52 (5) 9.94 (5) 81 0.024 (5) (4) 31 55 (3) (8) (6) (1) 9.94 (4) 159 0.188 (4) (4) (14) (13) (2) (7) (1) (1) (1) traction time 1 h, vacuum application step omitted 9.91 (10) 61 0.031 (4) (5) 36 106 (9) (8) (24) (1) 9.94 (5) 86 0.037 (6) (3) (6) (3) (6) (3) (1) (3) (2) (3) (1) 9.94 (5) 86 0.037 (6) (3) (6) (3) (6) (8) (1) (3) (2) (3) (1) (3) (2) (1) (1) e separated from ethylbenzene only with maximum sensitivity (cf. text); \ddagger n.d. = not detected, <i>i.e.</i> , not evident or <25 ppm	0°C, extraction time 1 h, vacuum appl	action time 1 h, vacuum appl	ne 1 h, vacuum appl	uum appl	Ы	ication s	tep omitte							,			× •	
9.94 (5) 81 0.024 (5) (4) 31 55 (3) (8) (6) (1) 9.94 (4) 159 0.188 (4) (4) (13) (2) (7) (1) (1) (1) 9.94 (4) 159 0.188 (4) (4) (14) (13) (2) (7) (1) <td>9.94 (5) 81 0.024 (5) (4) 31 55 (3) (8) (6) (1) 9.94 (4) 159 0.188 (4) (4) (14) (13) (2) (7) (1) (1) (1) 9.94 (4) 159 0.188 (4) (4) (14) (13) (2) (7) (1)</td> <td></td> <td>87 7 9</td> <td><u>6</u></td> <td>9</td> <td>ð.</td> <th>9.87</th> <td>(4)</td> <td>39</td> <td>0.083</td> <td>E</td> <td>(8)</td> <td>45</td> <td>159</td> <td>ව</td> <td>(12)</td> <td>52</td> <td>(2)</td> <td></td>	9.94 (5) 81 0.024 (5) (4) 31 55 (3) (8) (6) (1) 9.94 (4) 159 0.188 (4) (4) (14) (13) (2) (7) (1) (1) (1) 9.94 (4) 159 0.188 (4) (4) (14) (13) (2) (7) (1)		87 7 9	<u>6</u>	9	ð.	9.87	(4)	39	0.083	E	(8)	45	159	ව	(12)	52	(2)	
9.94 (4) 159 0.188 (4) (14) (13) (2) (7) (1)	9.94 $ $ (4) 159 0.188 (4) (4) (14) (13) (2) (7) (1) (1) (1) (1) (12 citraction time 1 h, vacuum application step omitted 9.91 $ $ (10) $ $ 61 $ $ 0.031 $ $ (4) $ $ (5) $ $ 36 $ $ 106 $ $ (9) $ $ (8) $ $ (24) $ $ (1) $ $ 9.94 $ $ (5) $ $ 86 $ $ 0.037 $ $ (6) $ $ (3) $ $ (6) $ $ (8) $ $ (1) $ $ (3) $ $ (3) $ $ (1) $ $ (1) $ $ e separated from ethylbenzene only with maximum sensitivity (cf: text); \ddagger n.d. = not detected, <i>i.e.</i> , not evident or <25 ppm		80 6	6	ð	ð,	9.94	(S)	81	0.024	ં	(4)	31	55	3	8	ම	Ξ	
9.91 (10) 61 0.031 (4) (5) 36 106 (9) (8) (24) (1) 9.94 (5) 86 0.037 (6) (3) (6) (8) (1) (3) (1)	xtraction time 1 h, vacuum application step omitted 9.91 (10) 61 0.031 (4) (5) 36 106 (9) (8) (24) (1) 9.94 (5) 86 0.037 (6) (3) (6) (3) (7) (3) (1) (3) (3) (1) esparated from ethylbenzene only with maximum sensitivity (cf. text); \ddagger n.d. = not detected, <i>i.e.</i> , not evident or <25 ppm	0 0.42 84 3 9	84 3 9	3 	6	9	9.94	(4)	159	0.188	(4)	(4)	(14)	(13)	(7)	E	Ξ	Ξ	
99.91 (10) 61 0.031 (4) (5) 36 106 (9) (8) (24) (1) 99.94 (5) 86 0.037 (6) (3) (6) (8) (1) (3) (3) (1)	99.91 (10) 61 0.031 (4) (5) 36 106 (9) (8) (24) (1) 99.94 (5) 86 0.037 (6) (3) (6) (8) (1) (3) (1) 99.94 (5) 86 0.037 (6) (3) (6) (8) (1) (3) (1) (1) be separated from ethylbenzene only with maximum sensitivity (cf text); $\ddaggerd. = not detected, i.e., not evident or <25 ppm$	1-90°C, benzene extraction at 110°C,	nzene extraction at 110°C,	traction at 110°C,	110°C;		extraction	time 1 h,	vacuum ap	plication	i step omi	tted	·						
	be separated from ethylbenzene only with maximum sensitivity (cf. text); ‡n.d. = not detected, i.e., not evident or <25 ppm	84 8 86 4	84 8 86 4	8 4			99.91 99.94	(<u>1</u> 0)	61 86	0.031	6)	ତତ	છ લ	® <u>1</u> 8	<u>ھ</u>	<u>@</u>	(24) (3)	ΞΞ	

724 P. Becker-Heidmann, A. Hiller and J. Hofmann

importance and ordinarily <25 ppm. If present, phenol occurred only at much less than 10 ppm. In many analyses, some non-identifiable compounds could be observed. While some of these compounds appeared at a very low retention time in the gas chromatogram (altogether up to 250 ppm) and could be related to dissolved remains of aliphatic hydrocarbons, others with higher retention time (maximum 50 ppm each) probably relate to additional substituted aromatic compounds. Obviously, the spectrum of trace compounds in the benzene varied significantly from sample to sample, even with the same reaction conditions, agreeing with Witkin *et al.* (1993), but disagreeing with Switsur and Waterhouse (1989).

Increasing the temperature of the benzene extraction from 180 to 230°C did not result in substantial differences of yield and purity. Ongoing investigations have resulted in reproducible benzene purity of *ca.* 99.9% or better by 1) reducing the temperature of benzene removal from the catalyst, *e.g.*, extracting at 110°C for 1 h without the vacuum application step, and 2) increasing the temperature of the acetylene-catalyst reaction to 80–90°C (*cf.* Table 4). The high yield and purity at increased temperature is an unexpected result, because the trimerization reaction of acetylene to benzene is an exothermic reaction (Tamers 1975). An explanation may be given in case of a low acetylene inflow rate and an excess surface area, which holds true for the PK200Tr used in these experiments, where an increased reaction temperature can prevent coupling of acetylene molecules to the surface too far from each other to trimerize. Such modified reaction conditions reveal further improvements: The number of by-products with concentrations >25 ppm are limited to 8 components. Oxygen-containing impurities never exceed 15 ppm acetone and 5 ppm acetaldehyde. By means of air purging of the extracted benzene for a few seconds, the total content of low-retention-time contaminants can be kept <100 ppm.

CONCLUSION

The most important result of our studies is that the PK200Tr catalyst with 0.05% chromium endowment and 450 m²g⁻¹ specific surface area does not differ significantly regarding yield and purity of synthesized benzene from the original catalyst PKN/D1, with 0.10% Cr and 225 m²g⁻¹, under reaction conditions of both the Leipzig and Hamburg ¹⁴C laboratories. The yield was reproducible *ca*. 87 ± 2% related to sample-derived acetylene (>90% related to pure tank acetylene), and the purity of the benzene was between 99.4 and 99.95% (mean value ~99.8%) for both catalysts. The determined contaminants were exclusively hydrocarbons, which produce no quench effects in LS spectrometry in the measured concentrations. Replacing the original PKN/D1 with the PK200Tr, with half the chromium endowment but doubled specific surface area, is no disadvantage to normal-precision ¹⁴C dating. The best results, *i.e.*, the highest benzene purity, can be obtained by slow acetylene absorption and benzene extraction at a temperature up to 110°C for 1 h without the succeeding vacuum application step.

ACKNOWLEDGMENTS

We thank I. Briese and U. Günther for benzene syntheses and discussions, H.-M. Nitzsche and S. Franke for GC analyses, P. Bertelmann for GC/MS analyses, K. H. Kampmann of Solvay Catalysts, Hannover, for delivering the catalyst samples, and G. H. Lietz of Commercia Chemie GmbH, Hannover, for submitting the catalyst specifications and additional samples. We also thank M. Tamers for discussion and J. E. Noakes for critically reviewing the manuscript.

REFERENCES

- Noakes, J. E., Kim, S. M. and Stipp, J. J. 1965 Chemical and counting advances in liquid scintillation age dating. In Chatters, R. M. and Olson, E. A., eds., Proceedings of the 6th International Conference Radiocarbon and Tritium Dating. Clearing House for Federal Scientific and Technical Information, NBS, U.S. Department of Commerce: 68–91.
- Pietig, F. and Scharpenseel, H. W. 1966 Altersbestimmung mit dem Flüssigkeits-Szintillations-Spektrometer. - Ein neuer Katalysator zur Benzolsynthese. Atompraxis 12: 95-97.
- Switsur, R. and Waterhouse, J. S. 1989 Benzene purity in radiocarbon dating samples. *In* Long, A., Kra, R. S.

and Srdoč, D., eds, Proceedings of the 13th International ¹⁴C Conference. *Radiocarbon* 31(3): 260–263.

- Tamers, M. 1975 Chemical yield optimization of the benzene synthesis for radiocarbon dating. International Journal of Applied Radiation and Isotopes 26: 676– 682.
- Witkin, D., Kalin, R. M., Long, A., Rigali, M. J. and Nagy, B. 1993 Production of impurities in benzene synthesis for liquid scintillation counting and its effect on highprecision radiocarbon measurements. *In* Noakes, J. E., Schönhofer, F. and Polach, H. A., eds, *Liquid Scintillation Spectrometry 1992*. Tucson, Arizona, Radiocarbon: 115–124.