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

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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 KaliChemie[4]) 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 $SrCO_3$, 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,

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

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

Catalyst variety	Cr endowment (% of weight)	Specific surface area (m^2g^{-1})
PKN/D1	*ca.* 0.10	225 ± 25
PK200Tr	*ca.* 0.05	450 ± 50
PKN/D0	0	225 ± 25
PKN/D9	*ca.* 0.1	*ca.* 120

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 N_2 and O_2 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 μm 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.

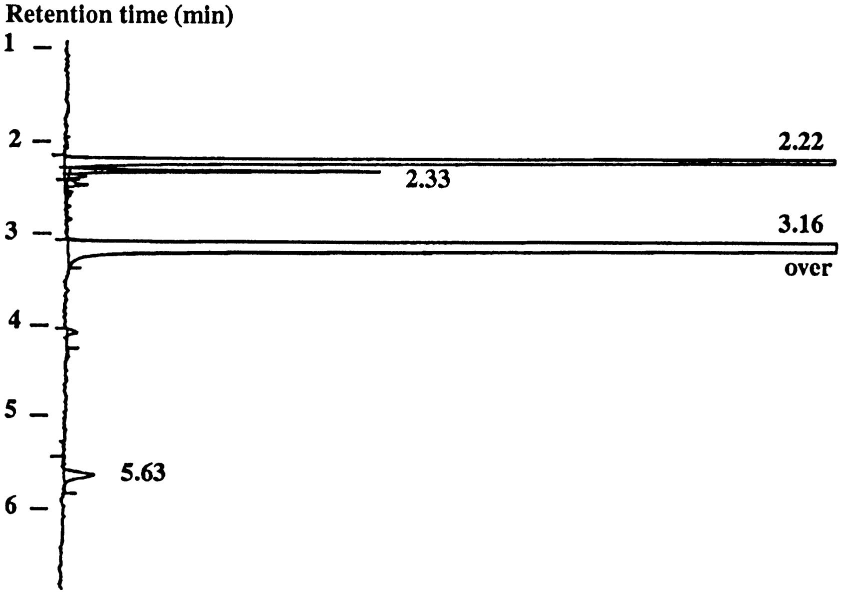

Fig. 1. Gas chromatogram of a sample prepared with PKN/D0 catalyst. All numbers are retention times. The peak at 3.16 min belongs to benzene. The peak at 2.22 min is 3.1%; the one at 2.33 min is 0.0082% of the benzene peak area in size. Neither compound was identified.

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 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.

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

	0.1 Cr		0.05 Cr	
	PKN/D1	PKN/D1	PKN200Tr	PKN200Tr
Yield (%)	90.5	97.4	95.5	95.0
Benzene purity (%)	>99.99	>99.99	99.57	99.58
Toluene (%)	0.001	0.002	0.010	0.010
Ethylbenzene/ Xylene (%)	<0.001	<0.001	0.023	0.026
C_3-benzenes (%)	<0.001	<0.001	0.004	0.002
C_4-benzenes (%)	<0.001	<0.001	0.002	0.001
C_5-benzenes (%)	<0.001	<0.001	0.001	0.001
Naphthalene (%)	<0.001	0.001	0.003	0.002

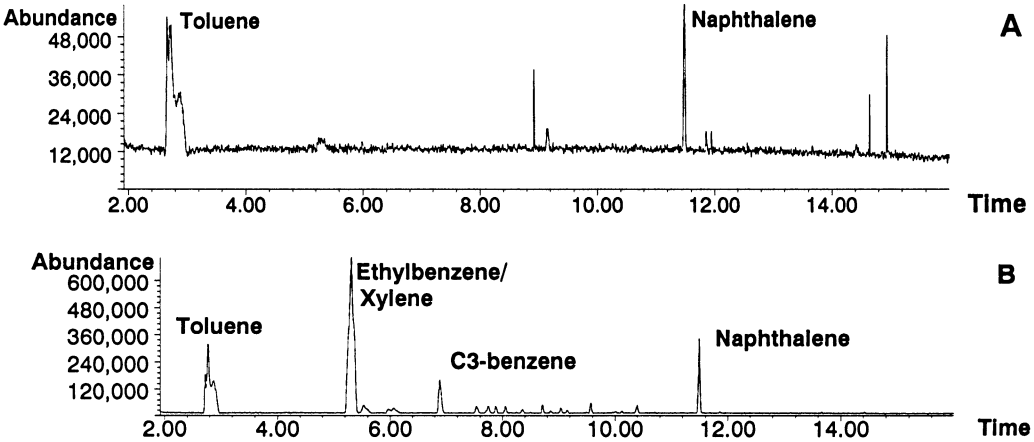

Fig. 2. GC/MS spectra of impurities of benzene produced from tank acetylene: A. with PKN/D1; B. with PK200Tr

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 Benzene Synthesized from Acetylene Mixed with Different Amounts of Ethylene

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

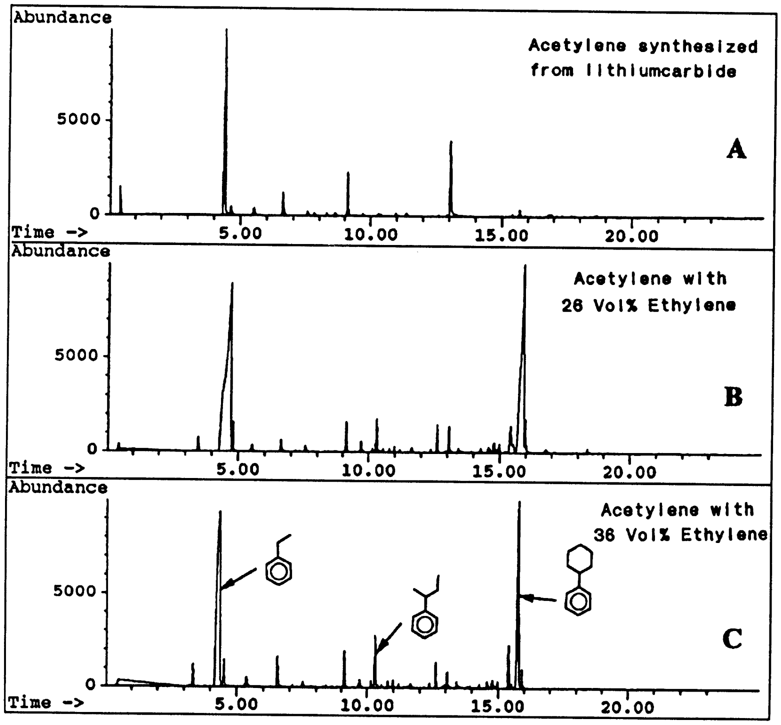

Fig. 3. GC/MS spectra of impurities of benzene produced from: A. a normal sample; B. acetylene with 26% vol. ethylene; C. acetylene with 36% vol. ethylene

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 ± 2%, showing no influence of conditions nor of catalyst type.

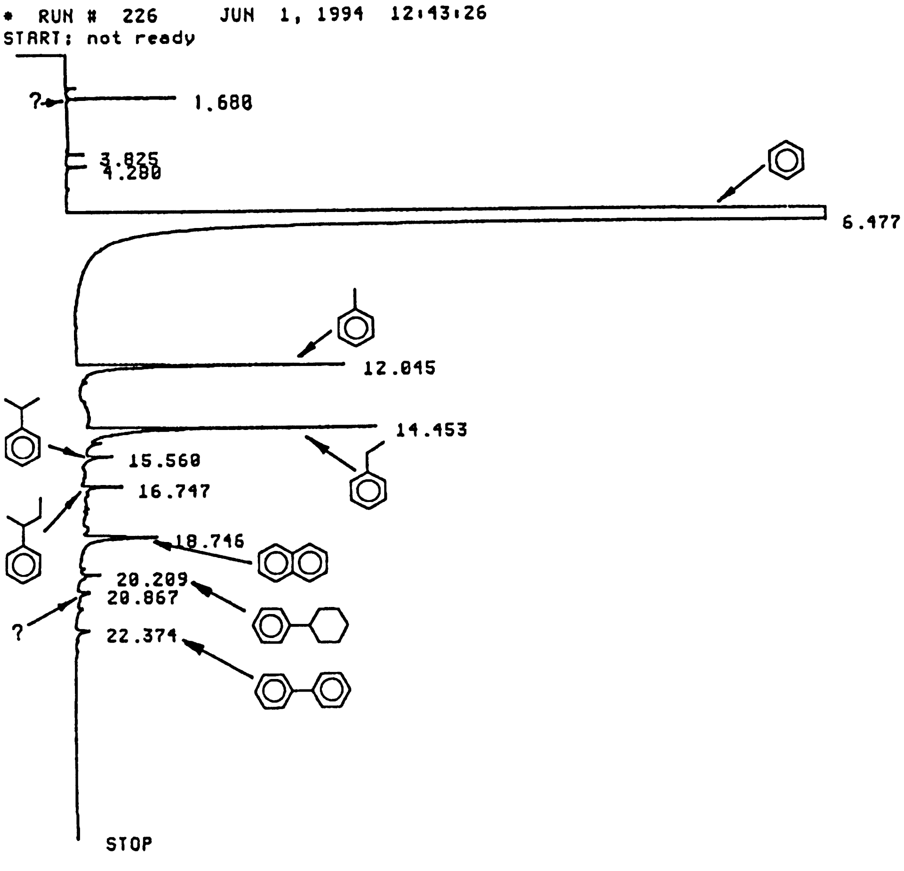

Fig. 4. Typical gas chromatogram of synthesized benzene recorded with medium sensitivity and showing the most important impurities

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

TABLE 4. Trace components of benzene synthesized with PK200Tr and with PKN/D1 (in italics) under varied Leipzig laboratory conditions. Concentrations <25 ppm in parentheses.

Lab no.*	GC acetylene analysis			Ben-zene yield	Total number of comp. >25		BEN-ZENE	TRACE COMPONENTS**											Ben-zene content (MS)
	C_2H_2 [%]	C_2H_4 [%]	C_2H_6 [%]	[%]	ppm		[%]	Acetone [ppm]	Toluene [ppm]	Ethyl-benz. [%]	m-/p-xylene [ppm]	o-xylene [ppm]	Isopr.-benz. [ppm]	Isobu. benz. [ppm]	Diethyl benz. [ppm]	Naph-thal. [ppm]	Cyclo-hexyl-benz. [ppm]	Bi-phenyl [ppm]	[%]
						Mol-wt.:	78	58	92	106	106	106	120	134	134	128	160	154	
Normal conditions																			
LZ-1105	*99.4*	*0.40*	*0.11*	*87*	*9*		***99.76***	*(11)*	*120*	*0.183*	*?†*	*n.d.‡*	*40*	*211*	*n.d.*	*91*	*68*	*n.d.*	*99.87*
LZ-1046				86	9		**99.84**	n.d.	110	0.075	?	(9)	101	59	*ca.* 60	151	73	n.d.	
LZ-1073				89	13		**99.44**	(8)	280	0.436	?	(14)	86	316	26	126	129	n.d.	
LZ-1109				87	11		**99.82**	n.d.	150	0.096	?	n.d.	58	172	n.d.	136	163	66	
LZ-1112				86	5		**99.94**	(7)	(12)	0.012	(19)	(10)	(14)	40	(5)	36	59	(19)	
Reduced reaction time (*ca.* 10 min)																			
LZ-1108	*99.8*	*0.12*	*0.03*	*87*	*9*		***99.91***	*n.d.*	*131*	*0.047*	*?*	*n.d.*	*40*	*76*	*n.d.*	*119*	*33*	*42*	
LZ-1075				87	16		**99.48**	(15)	207	0.351	90	27	104	446	30	49	198	53	
LZ-1076				87	13		**99.43**	(8)	237	0.423	(16)	(22)	74	274	(21)	156	178	37	
LZ-1157				86	9		**99.80**	(7)	158	0.116	(23)	(17)	76	130	(21)	30	61	(7)	
Extended reaction time (up to *ca.* 30 min)																			
LZ-1084				87	11		**99.84**	(19)	233	0.064	105	n.d.	60	152	n.d.	118	76	30	
LZ-1089	96.7	2.03	1.09	87	11		**99.86**	n.d.	130	0.066	?	n.d.	45	174	n.d.	72	132	35	
Vacuum application step after extraction omitted																			
LZ-1106	*99.7*	*0.17*	*0.03*	*86*	*4*		***99.96***	*n.d.*	*145*	*0.026*	*?*	*n.d.*	*n.d.*	*(22)*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*99.97*
LZ-1096				89	7		**99.89**	n.d.	199	0.071	?	n.d.	34	34	n.d.	109	n.d.	n.d.	
LZ-1097				87	8		**99.90**	(10)	195	0.047	?	n.d.	30	39	(19)	34	n.d.	n.d.	
LZ-1100				86	8		**99.89**	(7)	72	0.079	?	n.d.	31	50	(12)	44	29	(17)	
Tap-water cooling																			
LZ-1107	*99.6*	*0.25*	*0.09*	*87*	*7*		***99.91***	*n.d.*	*81*	*0.053*	*?*	*n.d.*	*30*	*95*	*n.d.*	*104*	*46*	*37*	*99.94*
LZ-1093	99.5	0.32	0.06	87	12		**99.71**	96	157	0.143	?	n.d.	110	439	n.d.	101	247	n.d.	
LZ-1099				87	8		**99.83**	n.d.	286	0.079	?	(11)	58	133	(13)	130	46	(23)	
Benzene extraction at 110°C, extraction time 1 h, vacuum application step omitted																			
LZ-1130				87	7		**99.87**	(4)	39	0.083	(7)	(8)	45	159	(9)	(12)	52	(5)	
LZ-1132	99.6	0.28	0.09	86	6		**99.94**	(5)	81	0.024	(5)	(4)	31	55	(3)	(8)	(6)	(1)	
LZ-1137	96.5	2.90	0.42	84	3		**99.94**	(4)	159	0.188	(4)	(4)	(14)	(13)	(2)	(7)	(1)	(1)	
Reaction temperature 80-90°C, benzene extraction at 110°C, extraction time 1 h, vacuum application step omitted																			
LZ-1152				84	8		**99.91**	(10)	61	0.031	(4)	(5)	36	106	(9)	(8)	(24)	(1)	
LZ-1159				86	4		**99.94**	(5)	86	0.037	(6)	(3)	(6)	(8)	(1)	(3)	(3)	(1)	

*LZ = Leipzig;** analytical error < ±5 %; †? = uncertain; can be separated from ethylbenzene only with maximum sensitivity (*cf.* text); ‡n.d. = not detected, *i.e.*, not evident or <25 ppm 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 m^2g^{-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 m^2g^{-1}, under reaction conditions of both the Leipzig and Hamburg ^{14}C 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 ^{14}C 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.

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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 ^{14}C 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 high-precision radiocarbon measurements. *In* Noakes, J. E., Schönhofer, F. and Polach, H. A., eds, *Liquid Scintillation Spectrometry 1992*. Tucson, Arizona, Radiocarbon: 115–124.