

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry



journal homepage: www.elsevier.com/locate/fluor

Preparation of cis-1,1,1,4,4,4-hexafluorobut-2-ene by cis-selective semi-hydrogenation of perfluoro-2-butyne

Xiaoqing Jia^a, Xiaomeng Zhou^b, Hengdao Quan^{b,*}, Masanori Tamura^b, Akira Sekiya^b

^a Beijing Institute of Technology, Beijing 100081, China

^b National Institute of Advance Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

ARTICLE INFO

Article history: Received 31 March 2011 Received in revised form 28 May 2011 Accepted 4 June 2011 Available online 13 June 2011

Keywords: Cis-1,1,1,4,4,4-hexafluorobut-2-ene Perfluoro-1,3-butadiene Semi-hydrogenation Pd-based catalyst Porous aluminum fluoride

ABSTRACT

Cis-1,1,1,4,4,4-hexafluorobut-2-ene has a zero ozone depletion potential (ODP), low global warming potential (GWP) and non-flammable properties, so it is believed to be a potential foam expansion agent. For the synthetic process of cis-1,1,1,4,4,4-hexafluorobut-2-ene, the process catalysts are the key factors for its yield and cost. In this paper, the catalysts of palladium attached to porous aluminum fluoride, to active carbon, to Al₂O₃, and the blends of palladium and bismuth to AlF₃ used to prepare cis-1,1,1,4,4,4-hexafluorobut-2-ene by cis-selective semi-hydrogenation of perfluoro-2-butyne were investigated. The performance of above-mentioned catalysts was compared in reaction process. The experimental results indicate that the additive of bismuth to palladium catalyst is useful for improving the activity and selectivity compared to Pd/C and Pd/Al₂O₃. The role of bismuth in the synthetic process is discussed based on the experimental results and theory analysis.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

In these years, much attention has been paid on the global warming problem. The chlorofluorocarbons (CFCs) or hydrochlorofluorocarbons (HCFCs) are considered to be the main compounds in the contribution to global warming. Hydrofluoroolefines (HFOs), as the prime alternatives of CFCs, HCFCs and HFCs used as coolants, blowing agents, cleaners have been studied and selected due to their low global warming potential (GWP) and zero ozone depletion potential (ODP). Meanwhile, the facile synthetic route for preparing HFOs has been investigated in industry [1].

Cis-1,1,1,4,4,4-hexafluorobut-2-ene is a non-ozone depleting compound with an acceptable GWP. Its short lifetime in atmosphere indicates that it is not a long lived atmospheric breakdown product. Furthermore, this compound is not a volatile organic compound, and it is low toxicity and is non-flammable, with a boiling point of 33 °C. Besides that, the study in DuPont company shows that cis-1,1,1,4,4,4-hexafluorobut-2-ene is characterized by good compatibility and chemical stability in generic foam systems and foam processing materials. So it is used as "Fourth-Generation" foam expansion agent [2]. For the synthetic method of cis-1,1,1,4,4,4-hexafluorobut-2-ene, some liquid phase methods have been developed. For example, Lui et al. [3] had developed a method that prepared 1,1,1,4,4,4-hexafluorobut-2-ene from CF₃–CH₂–CHCl–CX₃, in which the individual radicals X independently of each other represent chlorine and/or fluorine, by reaction with alkali metal fluoride in an aprotic polar solvent. Aoyama et al. have prepared cis-1,1,1,4,4,4-hexafluorobut-2-ene and trans-1,1,1,4,4,4-hexafluorobut-2-ene using 1,1,1-trifluoro-2,2-dichloroethane, amine and copper as raw materials [4]. However, by these liquid phase method, the yield rate of cis-1,1,1,4,4,4-hexafluorobut-2-ene is low. The synthetic process is a batch reaction and have a serious pollution besides the synthesize apparatus is complex. For vapor phase synthetic method of cis-1,1,1,4,4,4-hexafluorobut-2-ene, there is rare report until now [5].

In our laboratory, a vapor-phase method in continuous process to prepare cis-1,1,1,4,4,4-hexafluorobut-2-ene by cis-selective semi hydrogenation of CF_3CCCF_3 is developed. We found that the process catalyst is the key effect factor for the synthesis of cis- $CF_3CHCHCF_3$. The catalysts of palladium attached to porous aluminum fluoride, to active carbon, to Al_2O_3 , the blends of palladium and Bi attached to AIF_3 to prepare cis-1,1,1,4,4,4hexafluorobut-2-ene by cis-selective semi-hydrogenation of perfluoro-2-butyne were investigated in this paper. The performance of the catalysts and the catalytic mechanism of bismuth in the synthetic process is discussed based on the experimental results and theory analysis.

^{*} Corresponding author. Tel.: +81 298 614657; fax: +81 298 614657. *E-mail address*: Hengdao-quan@aist.go.jp (H. Quan).

^{0022-1139/\$ –} see front matter \circledcirc 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jfluchem.2011.06.004

2. Experimental

2.1. Chemicals

CF₂=CFCF=CF₂ (95% purity) was purchased from Kanto Chemical Co. Porous aluminum fluoride (PAF) was obtained from Xi an Modern Chemistry Research Institute, Xi'an, China. 5.0% Pd/C (surface area 971.70 m²/g), 3% Pd/AlF₃ (surface area 7.77 m²/g), 2.0% Pd + 0.1% Bi/PAF (surface area 9.02 m²/g), 4.5% Pd + 0.5% Ag/C (surface area 918.86 m²/g), 1% Pd/(γ -Al₂O₃) (surface area 35.58 m²/g), 0.5% Pd/C (surface area 1151.74 m²/g) are used in experimental process.

2.2. Instrument

Apparatus for investigating the reaction process of CF_3CCCF_3 and H_2 consist of N_2 mass flow controllers, an electrically heated tubular type-316 stainless-steel reactor, 12 mm in diameter and 300 mm in length.

The BET surface area of 5.0% Pd/C, 3% Pd/AIF₃, 2.0% Pd + 0.1% Bi/ PAF, 4.5% Pd + 0.5% Ag/C, 1%Pd/(γ -Al₂O₃), 0.5% Pd/C were measured by means of low temperature adsorption of nitrogen using a Micromeritics ASAP 2000. Samples were degassed under vacuum at 573 K for 3 h before measurement.

GC analysis was conducted on a Shimadzu GC-17 A. The capillary column was a CP-PoraPLOT Q with 0.32 mm i.d. and 53 m from J&W Scientific Inc. The column was programmed as follows: the initial temperature was set at 100 °C for 5 min; then the temperature was increased at the rate of 10 °C/min, and finally to 200 °C and held for 10 min.

MS (EI, 70 eV) spectra were measured using the Shimadzu GCMS-QP2010 system equipped with GC-2010. And the column type and the parameters were same as above mentioned GC conditions.

¹H NMR and ¹⁹F NMR of cis-CF₃CH=CHCH₃ and its intermediate were recorded on a JNM-EX300 spectrometer (JEOL, 300 MHz) at 25 °C with Me₄Si and CFCl₃, respectively, as internal references in CDCl₃ solvent.

2.3. Preparation of CF₃CCCF₃ from CF₂=CFCF=CF₂

CF₃CCCF₃ was prepared by CF₂=CFCF=CF₂ using AlOCIF as catalyst (as Scheme 1 shown). By a series of measuring, it is shown that at room temperature, the yield rate of CF₃CCCF₃ is up to 99.5%. If the reaction temperature rises to 200 °C, cyclocompounds appeared and the yield rate of CF₃CCCF₃ is decreased abruptly.

2.4. Preparation of above-mentioned catalysts

2.4.1. 0.5% Pd/C and 5.0% Pd/C

The activated charcoal was impregnated into a sufficient amount of palladium chloride solution overnight. The amount of palladium chloride in the solution was adjusted to give a final metal loading to 0.5 wt% and 5.0 wt% respectively. The saturated supporter was baked at 200 °C for 6 h and 300 °C for 6 h. The reduction of catalyst was run in following procedure: 200 °C for 6 h; 300 °C for 6 h; and 350 °C for 5 h, the rate of hydrogen was 7.5 ml/min, 9 ml/min and 20 ml/min individually. The finished catalyst was used to catalytic hydrogenation.

$$CF_2 = CF - CF = CF_2 \xrightarrow{Cat} CF_3 C = CCF_3 + F$$

$$1 \qquad 2$$

2.4.2. 3% Pd/AlF₃

The PAF was impregnated into a sufficient amount of palladium chloride solution overnight. The amount of palladium chloride in the solution was adjusted to give a metal loading about 3 wt%. The following treating procedure is as Section 2.4.1 shown.

2.4.3. 1% Pd/(γ -Al₂O₃)

According to the procedure described in Section 2.4.1, about 1.0 wt% palladium was loading to γ -Al₂O₃ and was used to catalytic hydrogenation after the reduction of catalyst was run.

2.4.4. 2.0% Pd + 0.1% Bi/PAF

Bimetallic Pd–Bi/PAF catalyst containing 2.0% Pd and 0.1% Bi were obtained from monometallic palladium catalysts by repeated impregnation of these systems with water solution of $Bi(NO_3)_3$ - $5H_2O$ according to the procedure described in Section 2.4.1.

2.4.5. 4.5% Pd + 0.5% Ag/C

Monometallic palladium catalyst was impregnated into an amount of palladium AgNO₃ solution overnight. AgNO₃ in the solution was adjusted to give a Pd–Ag alloy loading. The following treating procedure is as Section 2.4.1 shown.

2.5. Analytic results of intermediate and cis-CF₃CH=CHCF₃

2.5.1. CF₂=CF-CF=CF₂

Boiling point, 6.5 °C. Spectral data, MS peaks m/z (%): 162 [M⁺], 143 [M⁺-F], 124 [M⁺-2F], 112 [M⁺-CF₂], 93 [M⁺-CF₃], 74 [M⁺-CF₄], 69 [M⁺-C₃F₃], 31 [M⁺-C₃F₅].

NMR Chemical shifts: 19 F (-CF-), -153.7 ppm. 19 F (CF₂-), -120.9 ppm.

2.5.2. CF₃C CCF₃

Boiling point, $-24.6 \,^{\circ}$ C. Spectral data, MS peaks m/z (%): 162 [M⁺], 143 [M⁺-F], 124 [M⁺-2F], 112 [M⁺-CF₂], 93 [M⁺-CF₃], 74 [M⁺-CF₄], 69 [M⁺-C₃F₃], 31 [M⁺-C₃F₅].

NMR Chemical shifts: ¹⁹F (CF₃-), -53.5 ppm.

2.5.3. Cis-CF₃CH=CHCF₃

Boiling point, 33.5 °C. Spectral data, MS peaks m/z (%): 164[M⁺], 145 [M⁺-F], 113 [M⁺-CHF₂], 95 [M⁺-CF₃], 75 [M⁺-C₂HF₃], 69 [M⁺-C₃H₂F₃].

NMR Chemical shifts: 19 F (CF₃-), -60.6 ppm. 1 H (-CH=), 6.65 ppm.

2.5.4. Trans-CF₃CH=CHCF₃

Boiling point, 8.5 °C. Spectral data, MS peaks m/z (%): 164 [M⁺], 145 [M⁺-F], 126 [M⁺-2F], 113 [M⁺-CHF₂], 95 [M⁺-CF₃], 75 [M⁺-C₂HF₃], 69 [M⁺-C₃H₂F₃].

Chemical shifts: 19 F (CF₃-), -66.4 ppm. 1 H (-CH=), 6.95 ppm.

2.5.5. CF₃CH₂CH₂CF₃

Boiling point, 24.6 °C. Spectral data, MS peaks m/z (%): 147 [M⁺-F], 127 [M⁺-HF₂], 97 [M⁺-CF₃], 77 [M⁺-CHF₄], 69 [M⁺-C₃H₄F₃], 51 [M⁺-C₃H₃F₄], 27 [M⁺-C₂HF₆].

Chemical shifts: ¹⁹F (CF₃-), -68.3 ppm. ¹H (-CH₂-), 2.49 ppm.

3. The experimental results

The experimental results show that there were four products in semi-hydrogenation of perfluoro-2-butyne, CF_3CCCF_3 , trans-CF₃CHCHCF₃, $CF_3CH_2CH_2CF_3$ and cis-CF₃CHCHCF₃, respectively (as Scheme 2 shown). The related factors of conversion of CF₃CCCF₃ and selectivity of cis-CF₃CHCHCF₃ with catalysts were investigated in particularly.



Scheme 2. Route to prepare cis-CF₃CHCHCF₃.

3.1. Effect of Pd wt% to catalytic activity

In this part, Al_2O_3 , AlF_3 and active carbon was used as catalyst supporter respectively. From Table 1, it is known that the conversion of CF_3CCCF_3 increased gradually and the yield of cis- $CF_3CHCHCF_3$ (target products) decreased abruptly when the Pd wt% increased to 5.0 wt% from 0.5 wt% in the active carbon. By comparing the conversion of reactant and the selectivity of target product in three catalyst supporters, it is known that AlF_3 owns the highest catalyst activity and Al_2O_3 owns the highest selectivity of target product in 200 °C reaction temperature.

From Fig. 1, it is shown that the yield of production 3-5 have no obvious change with the reaction temperature increase. CF₃CH₂CH₂CF₃ is the mainly production in reaction process. The yield of cis-CF₃CHCHCF₃ is below 30% among all productions. Fig. 2 shows that the conversion of CF₃CCCF₃ and the yield of cis-CF₃CHCHCF₃ decreased with the temperature increase. It is different between the catalyst using carbon and Al₂O₃ as catalyst supporter.

Fig. 3 shows that the conversion of CF_3CCCF_3 and the yield of cis- $CF_3CHCHCF_3$ are growing up with the temperature increase.

3.2. Effect of different additives to catalytic activity

Table 2 presents the conversion and selectivity of the following catalysts: 2.0% Pd + 0.1% Bi/AlF₃, 4.5% Pd + 0.5% Ag/C and 4.5%

Table 1

The conversion of 2 and the selectivity of production 5 in different catalyst supporter and Pd wt%.

Entry	Catalyst	Reaction temp. (°C)	Conversion (%)	Selectivity (%)
1	5.0% Pd/C	200	78.7	39.6
2	0.5% Pd/C	200	60.5	85.3
3	3.0% Pd/AlF ₃	200	91.5	68.4
4	1.0% Pd/Al ₂ O ₃	200	84.5	90.4



Pd + 0.5% Cu/C. Regardless of the content of additives in the studied catalysts Pd/C and Pd/AlF₃, the conversion and selectivity of target product is improved greatly comparing the monometallic catalyst. The results in Table 2 indicated that 2.0% Pd + 0.1% Bi/AlF₃ own the highest conversion and selectivity in the cis-selective semi-hydrogenation of perfluoro-2-butyne.

Fig. 4 shows that the distribution of productions in different reaction temperature. When the reaction temperature is from 150 °C to 200 °C, the yield of cis-CF₃CHCHCF₃ arrives to 90%. Besides that, the conversion of CF₃CCCF₃ increased with the temperature increasing. When the reaction temperature is more than 200 °C, the conversion of CF₃CCCF₃ is quantitative. However, the yield of by-product of trans-CF₃CHCHCF₃ is growing up with the temperature increasing.

Figs. 5 and 6 show that the conversion and selectivity of 4.5% Pd + 0.5% Ag/C catalysts and 0.5% Cu + 4.5% Pd/C catalyst in the



Fig. 2. Catalyst 3.0% Pd/AlF₃.



Fig. 3. Catalyst 1.0% Pd/(γ-Al₂O₃).

X. Jia et al./Journal of Fluorine Chemistry 132 (2011) 1188-1193

Table 2
The conversion of 2 and the selectivity of production 5 using different additives.

Entry	Catalyst	Reaction temp. (°C)	Conversion (%)	Selectivity (%)
5	Pd+0.1% Bi/AlF ₃	200	98.7	90.2
6	4.5% Pd+0.5% Ag/C	200	84.4	57.6
7	0.5% Cu+4.5% Pd/C	200	73.6	74.1



Fig. 4. Catalyst (2.0% Pd + 0.1% Bi/AlF₃).

different reaction temperature. With the reaction temperature increasing, the conversion and selectivity is improved gradually. When the temperature is arrived 200 °C, the effect of reaction temperature to the conversion and selectivity is not sensitive. Although it is improved greatly comparing with monometallic palladium catalysts, the yield of target product using 4.5% Pd + 0.5% Ag/C catalysts and 0.5% Cu + 4.5% Pd/C catalyst is quite low. However, Bi/Pd systems, even containing a small amount of bismuth are characterized by the highest activity and select in this reaction.

3.3. The activity comparison of different catalysts

Figs. 7 and 8 show that the comparison of catalytic activity and selectivity of different catalysts. It is shown that additives play an important role for improving the activity and selectivity. When Bi was added to the Pd/PAF catalyst and Ag was added to the Pd/C



Fig. 5. Catalyst (4.5% Pd + 0.5% Ag/C).



Fig. 6. Catalyst 0.5% Cu + 4.5% Pd/C.

catalyst respectively, the results shown the conversion and selectivity were improved obviously with the addition of Bi to the Pd/PAF catalyst, the conversion of CF₃CCCF₃ reached 98.7% and the selectivity of cis-CF₃CHCHCF₃ reached 90.2% at 250 °C. But the improvement of the catalyst 4.5% Pd after adding 0.5% Ag and catalyst 4.5% Pd after adding 0.5% Cu was not so obvious. So 2.0% Pd + 0.1% Bi/AlF₃ is believed to be a perfect catalyst for the preparation of cis-CF₃CHCHCF₃ by cis-selective semi-hydrogenation of perfluoro-2-butyne.

4. Discussion

Comparison with Figs. 1–8, it shows that addition of appropriate Bi to Pd catalyst improves the conversion and selectivity in synthesis of cis-CF₃CHCHCF₃.

Cis-selective semi-hydrogenation of alkynes is an important step in organic synthesis. Lindlar catalyst [6] is the most popular catalyst for this reaction. The Lindlar catalyst is a Pd/CaCO₃ catalyst treated with lead acetate solution and used in the presence of 0.05–1 molar equivalent of quinoline. One wellestablished action of the quinoline is to inhibit alkene surface interactions, which results in an overall selectivity increase, a general concept in selective hydrogenation reactions. An undesired effect is that quinoline also competes with alkynes for Pd surface interaction, which reduce the overall reaction rate [7]. Besides that, quinoline owns strong odor and is very difficult to remove in synthesize process. Cis-CF₃CHCHCF₃ could also be prepared by perfluoro-2-butyne and H₂ on Raney nickel [8], the yield just contains cis-CF₃CHCHCF₃ and CF₃CH₂CH₂CF₃. The



Fig. 7. Profile of conversion of 1 on different catalysts and reaction temperature.



Fig. 8. Profiles of selectivity of 5 on different catalysts and at different temperature.

catalysts which prepared on borohydride exchange resin in methanol show high selectivity [9]. But pyrophoric property of Raney nickel and batch reaction makes it hard to get quantitative products. Recently, the research on palladium bimetallic systems characterized by higher activity and stability than in the case of monometallic systems has started [10]. Therefore, Bi was attached to process catalyst in cis-1,1,1,4,4,4hexafluorobut-2-ene synthesis in our laboratory.

Bismuth is a well-established promoter of noble based catalysts for the selective liquid phase oxidation of alcohols, aldehydes and carbohydrates with molecular oxygen [11]. When it used alone, Bismuth is not inactive for the concerned oxidation reactions, but when associated with the noble metal, it considerable increase the overall catalytic performances and the lifetime of catalysts. The origin of the promoting role of bismuth on the activity of Pd is still a matter discussion. However, the influence of the addition of a second metal to Pd/support systems on catalytic properties in the reaction of semi-hydrogenation of alkynes in the gas phase has not been studied thoroughly yet.

The interpretation to bimetallic palladium catalysts should include following aspects: electronic effects, geometric effects, the occurrence of mixed sites [12–14]. Thus the promoting effect of addition of Bi on selectivity is interpreted as follows. When applied to Pd–Bi alloys between an active component Pd and an inactive one Bi, it indicate the dilution in ensembles of smaller size of the active surface Pd by Bi. It is deduced that these smaller ensembles of Pd is less facilitate to activate the reactant(s). Besides that, the addition of Bi made Pd well-distributed in supporter AlF₃ and surface of AlF₃ appeared more flat terrace. The flat terraces or extended terraces were conductive to interaction of perfluoro-2-butyne and hydrogen.

The effect process is as Fig. 9 shown.

According to the experimental results and theory discussion with catalyst of 2.0% Pd + 0.1% Bi/PAF, we proposed the mechanism of the improvement of conversion and selectivity for the addition of Bi to Pd/AlF₃ catalyst are as follows: A geometric effect which results from the dilution of the Pd surface layer with Bi appeared make surface of AlF₃ more flat terrace, which enhanced the rate of cis-CF₃CHCHCF₃ formation. The data in Figs. 7 and 8 are consistent with this model.

Synthesis of cis-CF₃CHCHCF₃ could be divided into two steps, the isomerization of perfluoro-2-butyne and then hydrogenation, which is seen in Fig. 9. We deduced that



molecule preferred to react with hydrogen molecule adopted around palladium atoms located at flat terrace sites.



Fig. 9. Possible reaction mechanism in synthesis of cis-CF₃CHCHCF₃ on Pd/AlF₃ catalyst (a) without addition of Bi and (b) addition of Bi to Pd/AlF₃.

5. Conclusion

The synthesis of cis-1,1,1,4,4,4-hexafluorobut-2-ene using practical catalysts was introduced. We found that cis-selective semi-hydrogenation of perfluoro-2-butyne proceeds with well conversion of perfluoro-2-butyne and surprising selectivity of cis-1,1,1,4,4,4-hexafluorobut-2-ene on catalyst (2.0% Pd + 0.1% Bi)/AlF₃. While, 5.0% Pd/C, 3.0% Pd/AlF₃, 2.0% Pd + 0.1% Bi/AlF₃, 4.5% Pd + 0.5% Ag/C, 1.0% Pd/ γ -Al₂O₃, 0.5% Pd/C, 0.5% Cu + 4.5% Pd/C, 2% Pd(PdCl₂)/AlF₃, did not show this effect. As an addition metal on Pd-based catalyst, Bi was a good modifier for the cis-selective semi-hydrogenation of perfluoro-2-butyne reaction. The plausible catalysis mechanism of Pd–Bi/AlF₃ in hydrogenation of perfluoro-2-butyne reaction was proposed.

References

- G. Loh, J.A. Creazzo, M.L. Robin, in: Proceedings of 12th Blowing Agents and Faoming Process, Cologne, Germany, 2010.
- [2] (a) G. Loh, J.A. Creazzo, M.L. Robin, DuPontTM Formacel WHITE PAPER, 2009;
 (b) H.-D. Quan, H.-E. Yang, M. Tamura, A. Sekiya, J. Fluorine Chem. 128 (2007) 190–195.
- [3] N. Lui, A.M. Leverkusen, D. Bielefeldt, U.S. Patent 5,463,150 (1995).
- [4] H. Aoyama, Osaka, U.S. Patent 5,516,951 (1996).
- [5] E.L. Dupont, P.C.T./U.S. Patent 2,009,037,459 (2009).
- [6] (a) H. Lindlar, Helv. Chim. Acta 35 (1952) 446-450;
- (b) O. Isler, A. Ronco, W. Guex, N.C. Hindley, W. Huber, K. Dialer, M. Kofler, Helv. Chim. Acta 32 (1949) 489–505;
- (c) J. Rajaram, A.P.S. Narula, H.P.S. Chawla, S. Dev, Tetrahedron 39 (1983) 2315–2322.

- [7] R. Cosmo, T.W. Hambley, S. Sternhell, J. Org. Chem. 52 (1987) 3119–3123.
 [8] A.L. Henne, W.G. Finnegan, J. Am. Chem. Soc. 71 (1949) 298–300.
 [9] J. Choi, N.M. Yoon, Tetrahedron Lett. 37 (1996) 1057–1060.

- [10] J. Petro, Contact Catalysis, Elsevier, Amsterdam, 1976.
- [11] M.Wenkin, P.Ruiz, B.Delmon, M. Devillers, J. Mol. Catal. A: Chem. 180(2002)141–159.
- [12] B. Coq, F. Figueras, J. Mol. Catal. A: Chem. 173 (2001) 117–134.
 [13] J.C. Fuggle, F.U. Hillebrecht, R. Zeller, Z. Zolstroknierek, P.A. Bennett, C. Freiburg, Phys. Rev. B 27 (1983) 2145.
 [14] A. Borodzinski, R. Dus, R. Frak, A. Janko, W. Palczewska, in: Proceedings of the 6th
- International Congress on Catalysis, London, (1976), p. 151.