

Journal of Physics and Chemistry of Solids 65 (2004) 627-632

JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

www.elsevier.com/locate/jpcs

Carbonaceous deposits on alumina as catalysts and supports

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Accepted 19 August 2003

Abstract

Studies of carbonaceous deposits, intercalated within alumina pores, were carried out from the point of view of their catalytic activity for a number of reactions of alkyl-substituted benzenes. Alumina was not active for ammoxidation of ethylbenzene and *m*-xylene as well as oxidative dehydrogenation of ethylbenzene until certain amount of the deposit was generated on acid sites of alumina surface. Carbonaceous deposits formed during reactions of decomposition of 2-propanol and hexafluoro-2-propanol were used as supports for platinum catalysts for hydrosilylation of allyl chloride and 1-octene to result in excellent selectivity. Precursor of carbonaceous deposit formed from hexafluoro-2-propanol has been identified and scheme of the deposit formation was proposed. © 2003 Elsevier Ltd. All rights reserved.

Keywords: B. Chemical synthesis

1. Introduction

In reactions of organic compounds proceeding on oxide catalysts, secondary products in the form of carbonaceous deposit are often accumulated in the catalysts pores. Properties of the carbonaceous deposit depend on the nature of catalyst and reactants as well as reaction temperature. Carbonaceous deposits formed on oxide surfaces contain carbon, hydrogen and, in some cases, other elements as well. Hydrogen content decreases with increase in temperature and time on stream. At temperatures above 500 °C polyaromatic products accumulate on catalysts, whereas at lower temperatures condensation products of considerably lower C/H ratios are formed. Both forms of carbonaceous deposits are called coke by some authors, whereas the others use the term coke only for high-temperature products [1]. The deposition of coke is usually an undesirable phenomenon, because it leads to catalyst deactivation as a result of blocking the access to active centres. However, it was reported in the literature that a few cokes are catalytically active, e.g. carbonaceous deposits capable of catalysing reactions of oxidative dehydrogenation of alkylbenzenes [2-4] and ammoxidation of toluene [5]. The formation of coke can be also useful as a way of preparation of mixed-type catalyst supports and

carbon-mineral adsorbents [6,7] and catalysts [8]. Results of our earlier study on catalytic activity and selectivity of fluorinated carbon-supported platinum catalysts for hydrosilylation of alkenes and their derivatives [9] has encouraged us to investigate the performance of supports of mixed nature, such as fluorine-containing coke on alumina, in hydrosilylation reactions.

2. Experimental

2.1. Preparation of catalysts and their characterisation

Alumina (alu) was obtained by hydrolysis of aluminium isopropoxide followed by drying at 100 °C and calcining at 400 °C. Carbonaceous deposits (i-coke and f-coke) were formed in alumina pores by performing reactions of decomposition of 2-propanol (i) or hexafluoro-2-propanol (f) at 300 °C in a flow reactor. Catalysts containing 1%Pt on coke-covered alumina (Pt/i-coke and Pt/f-coke) were by incipient wetness method prepared using platinum acetylacetonate solution in chloroform, followed by three-hour reduction in hydrogen flow at 160 °C. The reduction temperature was established in preliminary TPR experiments performed on a Chemisorb 2705 apparatus (Micromeritics). Fluorine presence in f-coke was tested by XPS measurements carried out on a VG

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Scientific ESCA-3 photoelectron spectrometer and the identification of coke precursor formed as a result of hexafluoro-2-propanol decomposition on alumina was performed by GC/EI-MS technique on an AMD-402 two-sector mass spectrometer (AMD Intectra) of B/E geometry. High-resolution data were obtained on the same instrument by using V/E high-resolution scan. The compounds were introduced into the mass spectrometer using a gas chromatograph Hewlett-Packard Model 5890II. The instrument was equipped with a DB-1 fused-silica capillary column (J and W Scientific, $25 \text{ m} \times 0.2 \text{ mm i.d.}$). Flow rate of carrier gas (helium) was 1 ml/min and column temperature 40 °C. The GC/CI-MS analysis was performed on a Saturn 2160 GC/MS instrument (Varian). The GC parameters were the same as in the case of GC/EI-MS analysis, except for the column type which was DB-5.

Surface area and pore size distribution were determined on the ground of low-temperature nitrogen adsorption measurements performed on an ASAP 2010 soprtometer (Micromeritics).

2.2. Catalytic reactions

Ammoxidation of ethylbenzene and m-xylene was conducted in a flow reactor at 400 °C. Mole ratio of hydrocarbon:oxygen:ammonia was 1:5:2.5.

Oxidative dehydrogenation of ethylbenzene using nitrobenzene as a hydrogen acceptor was studied on coke catalysts obtained by passing different compounds through alumina at 450 °C. The coke precursors included parent compounds and products of the latter reaction, which differed considerably in their capability of forming carbonaceous deposits on alumina. Pulses of ethylbenzene/nitrobenzene mixture (mole ratio of 1:1) were injected into helium carrier gas flowing through microreactor loaded with coke-containing alumina. The reaction temperature was 450 °C and reaction products were transported by carrier gas to an on-line gas chromatograph.

Hydrosilylation of allyl chloride and 1-octene on Pt/coke catalysts was carried out in a batch reactor at 60 °C for 3 h followed by analysis of post-reaction mixture on a Perkin-Elmer Auto System XL gas chromatograph.

3. Results and discussion

Ammoxidation of ethylbenzene to benzonitrile and that of *m*-xylene to isophthalic acid dinitrile proceed on transition metal oxides such as vanadia and molybdena but not on alumina. The lack of activity for the above reactions in the case of pure alumina clearly results from Fig. 1 in which it is seen that at the initial period on stream, conversion to the above products is zero. However, alumina is well-known for its surface acidity and acid centres are the sites on which so-called coke, intercalated within alumina pores, is formed. This coke, as evidenced by the appearance and rise of activity



Fig. 1. Catalytic activity of carbonaceous deposit on alumina for ammoxidation of alkyl-substituted benzenes.

with increasing time on stream is the source of the catalytic activity, thus belonging to the family of carbonaceous deposits reported in the literature as catalytically active for a number of other reactions of ammoxidation and oxydehydrogenation [2-5]. Catalytic activity for both reactions, after a period of rise, reaches a quasi-stationary level, which represents equilibrium between the formation of coke and its deep oxidation to carbon oxides.

In our earlier paper [4] we have described the formation of carbonaceous deposit that was active for catalysing oxidative dehydrogenation of ethylbenzene with nitrobenzene to yield styrene and aniline as the reaction products. In the present study, we have generated carbonaceous deposit in alumina pores by passing separately parent compounds and products of the reactions through alumina bed in a reactor at 450 °C for 1.5 h (nitrobenzene, styrene, aniline) or 6 h (ethylbenzene). The reason for a longer time of alumina exposition to the latter compound was low formation of coke from ethylbenzene (0.7 wt% during 6 h, compared to 2.9, 3.5 and 10.2 wt% in the case of styrene, aniline and nitrobenzene, respectively, during 1.5 h). The study, aimed at determining which components of the reaction system discussed are the main contributors to the formation of catalytically active carbonaceous deposit, was performed by pulse technique which consisted in introducing pulses of the reactant mixture



Fig. 2. Catalytic activity for oxidative dehydrogenation of ethylbenzene with nitrobenzene shown by carbonaceous deposits formed from ethylbenzene, nitrobenzene, styrene and aniline.



Fig. 3. Chromatogram of the mixture collected after hexafluoro-2-propanol decomposition over alumina.

(ethylbenzene and nitrobenzene) onto pre-coked alumina. As concluded from Fig. 2, the highest catalytic activity was shown by coke of nitrobenzene origin, followed by that derived from aniline and styrene, whereas the activity of coke obtained from ethylbenzene was low. It is worth to add that the carbonaceous deposits prepared from nitrobenzene and aniline contained nitrogen, in addition to carbon and hydrogen. The C/N ratios in the above cokes were 9.7 and 9.1, respectively.

Next stage of the present study on the application of cokes intercalated within alumina pores to catalysis





consisted in the preparation of fluorine-containing coke that could serve as a support for hydrosilylation catalysts. Among supports reported for their use in reactions of In mass spectrum of compound 2 (Fig. 4), molecular ion was absent because in the case of fluorine-containing non-aromatic compounds, it easily undergoes fragmentation

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Fig. 4. EI-MS spectrum of compound 2.

 Table 1

 Textural characteristics of coke-containing alumina samples

Sample	Surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
alu	246	8.4	0.51
i-coke	213	9.0	0.48
Pt/i-coke	216	8.8	0.47
f-coke	30	12.2	0.09
Pt/f-coke	41	12.6	0.13

[13]. Ion of the highest m/z value (m/z 277) is formed by the elimination of fluorine from molecular ion, while that of m/z257 is a result of abstraction of fluorine atom and hydrogen fluoride molecule. The elimination of fluorine and carbon monoxide leads to ion of m/z 249. Fragment ion at m/z 199 has a low relative intensity, however, it is of significant importance to the confirmation of the structure of compound 2. It is formed from molecular ion as a result of the elimination of trifluoroacetyl radical. It is worth to add that in EI spectrum of compound 2, there are no ions created by elimination of other fluoroacetyl (di- or mono) radicals which confirms the proposed structure of compound 2. Ions observed in EI spectrum of compound 2 at m/z 195, 151 and 101 are formed as a result of skeletal rearrangements and a number of mechanisms leading to their formation can be proposed.

In order to find additional confirmation of the structure of compound **2**, we have carried out also high-resolution measurements for three ions of the highest m/z values in its

mass spectrum. The results are given in Table 1 and are in agreement with the interpretation of compound 2 fragmentation presented above. The GC/CI-MS analysis has also enabled to confirm molecular weight of compound 2.

After the identification of hexafluoro-2-propanol decomposition products, a question should be answered how the carbonaceous deposit is formed from them. Although alumina acidity is of Lewis-type and cokes formed on alumina surface are generated on Lewis acid centres, in the case of hexafluoro-2-propanol decomposition, hydrogen fluoride is evolved and a substitution of some of hydroxyl groups present on alumina surface with fluorine results in the appearance of Brønsted acid centres due to fluorine-induced weakening of O-H bond in the remaining hydroxyl groups. Acidic OH group (Brønsted acid site) donates proton to 4-(difluoromethyl)-4-hydroxyoctafluoropentan-2-one (compound 2) and the resulting species reacts with enol form of compound 1 (see the reaction scheme shown in Fig. 5) thus producing carbonaceous deposit. Such a structure cannot be long-lasting at temperature conditions of coke production process, therefore alumina covered with carbonaceous deposit should be removed from the reactor shortly after the deposit was formed. At prolonged exposure to elevated temperatures, aromatisation processes will proceed and fluorine and hydrogen loss will occur. The presence of fluorine in the carbonaceous deposit was confirmed by ESCA measurements which showed that there is no aluminium fluoride on the surface of alumina used in hexafluoro-2-propanol



Fig. 5. Scheme of formation of fluorine-containing carbonaceous deposit.

Table 2 Results of high-resolution measurements for ions of the highest m/z values in the EI-MS spectrum of the compound **2**

m/z		Error (ppm)	Composition
Calculated	Obtained		
276.9911	276.9897	5.1	C ₆ H ₂ O ₂ F ₉
256.9849	256.9847	0.8	C ₆ HO ₂ F ₈
248.9962	248.9972	-4.0	C ₅ H ₂ OF ₉

decomposition because binding energy (BE) was 74.3 eV, which is close to that of γ -alumina, boehmite and bayerite (74.2 eV), whereas in the case of AlF₃ it is 76.3 eV. The ratio of F/Al was 1.65 and that of O/Al was 1.47, which means that most of aluminium was bonded to oxygen and, therefore, the remaining amount of fluorine is bonded to carbon.

The decomposition of 2-propanol and hexafluoro-2propanol on alumina was carried out until roughly the same content of i-coke and f-coke (2.14 and 1.98 wt%, respectively) was reached and this required dosing 30times more 2-propanol than hexafluoro-2-propanol at the same feed flow rate (i.e. i-coke stayed in the reactor 30times longer than f-coke), because coke formation was much slower in the case of the former alcohol. In spite of similar coke content, surface area of alumina after becoming covered with f-coke decreased to a considerably greater extent than in the case of covering with i-coke (Table 2). This suggests that the formation of fcoke, which occurs much faster, takes place mostly at pore inlets, while i-coke probably fills alumina pores with more uniform layer.

The two cokes were investigated from the point of view of their performance as supports of platinum catalysts for addition of trichlorosilane to 1-octene and allyl chloride, i.e. reactions which are commercially exploited for the manufacture of adhesion promoters—3-chloropropyltrichlorosilane and octyltrichlorosilane. It can be seen in



Fig. 6. Activity of supported platinum catalysts for hydrosilylation of allyl chloride.



Fig. 7. Addition of trichlorosilane to 1-octene on supported platinum catalysts.

Figs. 6 and 7 that the use of carbonaceous deposit—mineral support results in obtaining excellent selectivity since no products other than desired ones (i.e. 3-chloropropyltrichlorosilane and octyltrichlorosilane, respectively) are formed in the presence of Pt/coke-covered alumina, contrary to Pt/alumina catalyst. In the case of hydrosilylation of allyl chloride (Fig. 6), not only selectivity, but also yield of desired product was higher when coke supports were used, particularly f-coke which is more hydrophobic. Surprisingly enough, a reduction in the yield of octyltrichlorosilane (Fig. 7) was observed in the case of the latter support (selectivity was still higher than on coke-free alumina support).

4. Conclusions

Carbonaceous deposits formed on acid sites of alumina in reactions of ammoxidation of alkyl-substituted benzenes belong to catalytically active cokes. Alumina itself is inactive for the above reactions.

Cokes formed in alumina pores by parent compounds and products of the reaction of oxydehydrogenation of ethylbenzene differ considerably in their catalytic activity for the above reaction, nitrobenzene-derived coke being the most active and that originated from ethylbenzene showing the poorest activity.

Decomposition of hexafluoro-2-propanol on alumina leads to the formation of 4-difluoromethyl-4-hydroxyoctafluoropentan-2-one which undergoes acid-catalysed conversion to fluorine-containing carbonaceous deposit.

Carbonaceous deposits on alumina, when used as supports for platinum, resulted in very selective catalysts for hydrosilylation of allyl chloride and 1-octene. The yield of desired products of both reactions carried out on Pt/i-coke surpassed that obtained on Pt/alumina, while in the case of Pt/f-coke it was higher only in the reaction of hydrosilylation of allyl chloride.

Acknowledgements

The authors wish to thank Dr Jerzy Stoch of the Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, for XPS measurements.

This study was supported by the State Committee for Scientific Research (Poland), Project No. 3 T09B 100 19.

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