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Selective side-chain oxidation of alkyl aromatic compounds catalyzed by cerium modified silver catalysts

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ABSTRACT

Silver supported on silica effectively catalyzes the aerobic side-chain oxidation of alkyl aromatic compounds under solvent-free conditions. Toluene, *p*-xylene, ethylbenzene and cumene were investigated as model substrates. Typically, the reaction was performed at ambient pressure; only for toluene an elevated pressure was required. Carboxylic acids, such as benzoic acid or *p*-toluic acid, additionally increased the reaction rate while CeO_2 could act both as a promoter and an inhibitor depending on the substrate and the reaction conditions. Silver catalysts were prepared both by standard impregnation and flame spray pyrolysis. Addition of a Ce precursor to the FSP catalyst resulted in significantly smaller silver particles. Ce-doped FSP catalysts in general exhibited a superior catalytic performance with TONs up to 2000 except for cumene oxidation that appeared to proceed mainly by homogeneous catalysis. In addition, flame-made catalysts were more stable against silver leaching compared to the impregnated catalysts. The structure of the silver catalysts was studied in detail both by X-ray absorption spectroscopy and transmission electron microscopy suggesting metallic silver to be required for catalytic activity. Catalytic studies point to a radical mechanism which differs depending on the type of substrate.

1. Introduction

Selective catalytic oxidation by inexpensive reagents such as oxygen, hydrogen peroxide or *t*-butyl hydroperoxide is a viable way of introducing functional groups and thereby upgrading saturated and unsaturated hydrocarbons [1–3]. Finding catalytic systems for these oxidation reactions is of significant industrial importance [4], e.g. for *p*-xylene and cyclohexane oxidation to terephthalic acid and adipinic acid, respectively, which are monomers for commodity polymers [5]. The high industrial impact is also reflected by the large amount of related patent literature (e.g. [6–8]). Nevertheless, these catalytic oxidation reactions still require harsh conditions in industry [4]. As an example, a very effective but highly corrosive and environmentally harmful homogeneous Co/Mn/Br system is employed for *p*-xylene oxidation [9] in liquid phase using acetic acid as solvent which is partly decomposed during reaction. The oxidation follows a radical chain mechanism with the transition metal promoting the chain initiation and the decomposition of peroxo species [4,9].

Active catalysts for the selective side-chain oxidation of alkyl aromatic compounds are reported mainly for liquid phase oxidations. Only a few examples are reported in the gas phase [10–12] or in supercritical media [13,14]. The selective liquid phase oxidation can be conducted both homogeneously and heterogeneously involving mostly metals with two or more stable oxidation states typically under acidic conditions. Most catalytic systems are based on Co often modified with Mn and a Br source [9,15,16] but other examples based on e.g. Pt [17] and Cu [18,19] are also known. Typical oxidizing agents are organic peroxides, hydrogen peroxide, and oxygen offering a cost-effective route to important industrial intermediates such as benzoic acid, acetophenone, benzophenone, toluic acid, etc. [5]. Interestingly, ring and side-chain oxidation can be controlled by the choice of oxidant [20,21]. Due to the relative inertness of the corresponding C–H bonds, the reactions are often performed at high pressure and in an additional solvent. Avoiding elevated pressure and working under neat conditions would be the next step to render the oxidation process more cost-efficient.

Based on the homogeneous Co/Mn/Br system used in the Amoco process many heterogeneous catalysts employ Co as a catalyti-

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Table 1
Overview over the silver catalysts prepared by flame spray pyrolysis and impregnation.

Catalyst	Ag (wt.%)	CeO_2 (wt.%)	SiO_2 (wt.%)	SSA (m^2/g)[a]	CeO_2 crystal size[b] (nm)	Ag crystal size[b] (nm)	Entry
$^{FSP}1\%Ag/SiO_2$	1	0	100	293	–	n.d.[c]	1
$^{FSP}1\%Ag/10\%CeO_2–SiO_2$	1	10	90	273	3.3	n.d.[c]	2
$^{FSP}1\%Ag/30\%CeO_2–SiO_2$	1	30	70	194	5.8	n.d.[c]	3
$^{FSP}1\%Ag/50\%CeO_2–SiO_2$	1	50	50	152	8.3	n.d.[c]	4
$^{imp}10\%Ag/SiO_2$-900	10	0	100	128	–	43	5

[a] Determined by nitrogen adsorption.
[b] Determined by XRD.
[c] Not detectable.

cally active metal. We were interested in the potential of silver as an active material as we showed recently that silver is a potent oxidation catalyst for the selective liquid phase oxidation of alcohols when used in combination with CeO_2 nanoparticles [22]. The impregnation route for catalyst synthesis afforded a broad silver particle size distribution with particles ranging from a few nm up to 50 nm. Flame spray pyrolysis (FSP) has extensively been studied for the preparation of different metal oxide catalysts [23,24] as well as supported noble metal catalysts often affording high metal dispersions with particle sizes of less than 5 nm on the support [25]. In this way, a good mixing of the oxide particles can be achieved. Therefore, we prepared in the present study the $Ag/SiO_2–CeO_2$ catalyst system not only by impregnation but also by single-step flame spray pyrolysis and investigated its potential for synthesis of catalysts for the oxidation of aryl aromatic compounds. Comparing $Ag/CeO_2–SiO_2$ catalysts made by these two routes, the FSP-made catalysts exhibited an improved performance even at significantly lower silver loadings for the oxidation of toluene, *p*-xylene, ethylbenzene and cumene. The structure was further elucidated by X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM).

2. Experimental

2.1. Catalyst synthesis

The impregnated catalyst was prepared by adding 25.0 mL of an aqueous $AgNO_3$ (Fluka, >99.5%) solution (31 mg/mL) to 5.00 g of SiO_2 (Aerosil 200, Degussa, 200 m^2/g) resulting in a $Ag:SiO_2$ ratio of 1:10. The mixture was stirred with a glass rod and sonicated for 1 h. After drying at 80 °C for 24 h the catalyst was calcined in air at 900 °C for 1 h in a muffle oven controlled by a Eurotherm 904 controller. The catalyst is denoted as $^{imp}10\%Ag/SiO_2$-900.

For catalysts made by flame spray pyrolysis, silver nitrate (Fluka, >99.5%) dissolved in ethanol (EtOH) and diethyleneglycol–monobutylether (DEGME, Fluka, >98%; 1:1, Ag 0.5 M), hexamethylsiloxane (HMDSO, Fluka >98%) and cerium-2-ethylhexanoate (40% Ce w/v, Strem) were used as silver, silica and ceria precursors, respectively. The appropriate amounts of the above mentioned precursor solutions were mixed with solvents, i.e. DEGME (Fluka, >98%) and 2-ethylhexanoic acid (Aldrich, >98%) while keeping the solvent composition constant at 1:1 by volume. The total support metal (Si + Ce) concentration was kept constant at 0.6 M in these solutions. The nominal CeO_2 weight fraction in the product powder ranged from 0 to 50 wt.%. The silver precursor was added accordingly to reach a nominal 1 wt.% Ag loading in the final powder product. The $Ag/CeO_2–SiO_2$ powders were produced in a laboratory scale FSP reactor as described elsewhere [26]. The liquid and dispersion gas feed rate were kept constant at 5 mL/min and of 5 L/min, respectively. The pressure drop above the nozzle was adjusted to 1.7 bar and a sheath gas flow of 5 L/min O_2 was applied through a metal ring (11 mm i.d., 18 mm o.d.) with 32 holes (0.8 mm i.d.) to ensure complete combustion of the precursor. The powders were collected with the aid of a vacuum pump (Busch SV 1025 B) on a glass microfiber filter (Whatman GF/D, 257 mm in diameter). The catalysts are denoted as $^{FSP}1\%Ag/SiO_2$ $^{FSP}1\%Ag/10\%CeO_2–SiO_2$, $^{FSP}1\%Ag/30\%CeO_2–SiO_2$ and $^{FSP}1\%Ag/50\%CeO_2–SiO_2$, respectively. Details are given in Table 1.

2.2. Catalyst testing

Catalyst tests were performed in a three-necked flask equipped with a gas inlet and a reflux condenser with *p*-xylene (Sigma–Aldrich >99%), ethylbenzene (Fluka, >99%) or cumene (Fluka, 98%) as substrates with and without CeO_2 nanoparticles (Aldrich, <25 nm), and benzoic acid (Sigma–Aldrich, 99%) or *p*-toluic acid (Aldrich, 98%). In a typical experiment the flask was charged with 122 mmol of alkyl aromatic compound and 100 mg biphenyl (Sigma–Aldrich, 99.5%) as internal standard. Biphenyl was unreactive under the applied reaction conditions, i.e. its presence did not give any additional peaks in the gas chromatogram. The flask was equipped with a magnetic stirring bar and placed in an oil bath heated to 140 °C which led to a temperature of the reaction mixture of ca. 135 °C. The mixture was saturated with oxygen (Linde, 99.95%) *via* the gas inlet and equilibrated for 1.5 h to ensure a uniform standard and substrate distribution. Benzoic acid (0.45 g, 3.7 mmol, 3.0 mol% with respect to the hydrocarbon; for ethylbenzene and cumene oxidation) and *p*-toluic acid (0.50 g, 3.7 mmol, 3.0 mol% with respect to the hydrocarbon; for *p*-xylene oxidation), respectively, were added. After 5 min a sample was taken for GC analysis and the reaction was started by adding 100 mg catalyst and optionally 50 mg CeO_2 (Aldrich, <25 nm) for catalysts not already containing CeO_2.

Analysis was carried out after 1, 2 and 3 h, respectively, by means of an Agilent 6890 N gas chromatograph equipped with a 7683 B series autosampler, a flame ionization detector and a HP-5 column using biphenyl as internal standard. The following temperature programs were used for product analysis: inlet temperature 250 °C; oven: 110 °C, hold for 10 min; ramp to 120 °C (5 °C/min); ramp to 300 °C (40 °C/min); 300 °C, 2 min; the analysis of hydroperoxides was performed at lower temperatures to ensure minimal decomposition during analysis: inlet temperature 100 °C; oven: 80 °C, hold for 10 min; ramp to 120 °C (5 °C/min); ramp to 300 °C (40 °C/min); 300 °C, 2 min. Products were identified by GC–MS. Individual response factors were obtained from commercial compounds, i.e. cumene hydroperoxide (Aldrich, 80% in cumene), *p*-methyl benzyl alcohol (Aldrich, 98%), *p*-methyl benzaldehyde (Aldrich, 97%), benzaldehyde (Aldrich, >99%), benzyl alcohol (SAFC, >99%), 2-phenyl-2-propanol (Aldrich, 97%), acetophenone (Aldrich, 99%) and 1-phenyl ethanol (Aldrich, 98%). Ethylbenzene hydroperoxide was synthesized according to Ref. [27] and the response factor determined from a mixture of 1-phenylethanol and ethylbenzene hydroperoxide.

Since starting material was lost during the reaction despite using reflux condensers, yields rather than conversions and selectivities are presented from which TONs are calculated on the basis of the total amount of silver. In general, results were reproducible within an error margin of 5–10%. Toluene required higher temperatures