Applied Catalysis A: General 470 (2014) 123–131

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Hydrogen-assisted dechlorination of $CF_3OCFCl–CF_2Cl$ to $CF_3OCF=CF_2$ over different metal-supported catalysts

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ARTICLE INFO

Article history:
Received 4 June 2013
Received in revised form
20 September 2013
Accepted 21 October 2013
Available online 30 October 2013

Keywords:
Activated carbon
Hydrodechlorination
Palladium
Copper

ABSTRACT

In this work the hydrogen-assisted dechlorination of $CF_3OCFClCF_2Cl$ to produce unsaturated $CF_3OCF=CF_2$ was studied over a series of metal catalysts supported on activated carbon. The results obtained indicated that the activity, stability, and selectivity of the materials were strongly dependent on the metal used. The activity of the monometallic catalysts follows the order Pd/C > Ru/C> Ni/C, while the sequence Ru/C > Ni/C > Pd/C was found for the selectivity to the target product. A wide diversity in reaction products was obtained with these materials. Pd-supported samples mainly yield saturated products. In contrast, $CF_3OCF=CF_2$ was the product most formed with Ru/C catalysts which, nevertheless, showed the lowest stability. However, when Ru or Cu was added to Pd catalysts, some very active, stable, and selective materials were obtained. Spent samples were characterized by TPD/MS, TGA, XRD, and FESEM techniques. The results obtained revealed that Ru-based catalyst deactivation was mainly due to the formation of heavy halogenated carbonaceous deposits.

1. Introduction

Catalysis is of crucial importance for the chemical industry and its use has traditionally been associated with chemical and refinery production. Today, catalysis is also an integral component in green processing technologies, serving as an important tool for sustainable development [1,2].

Since its development, PTFE has shown important chemical resistance properties, and in the second part of the twentieth century research was focused on studying fluorinated material properties and obtaining new kinds of polymers and materials by modifying fluorinated monomers. Within this framework, the role of substituents and ramifications proved important in obtaining specific properties such as gas permeability. As an example, perfluorovinylethers (i.e. $CF_3OCF=CF_2$) are important special monomers for fluorinated materials [3,4].

Today the trifluoromethyl trifluorovinyl ether ($CF_3OCF=CF_2$) commercial production process, based on $CF_3OCFClCF_2Cl$ precursor dechlorination [5], produces large quantities of by-products such as $ZnCl_2$, resulting in a significant cost to be calculated in the economic and environmental balance. A new approach, based on H_2-assisted gas-phase dechlorination over metal-supported catalysts, may lead to a new sustainable process.

Hydrodechlorination (replacement of selected halogen atoms with hydrogen) and hydrogen-assisted dechlorination (elimination of halogen atoms to form unsaturated compounds) has received much attention in the literature [6–9] as an option for the safe disposal of chlorofluorocarbon, as well as to produce valuable chemicals by either halogen substitution with hydrogen [10–12], or dechlorinated olefin formation [13,14]; however, very little is known about the use of hydrodechlorination to produce perfluorovinylethers.

Metal-based monometallic Ru, Pt or Pd catalysts were reported to be effective for the hydrodechlorination of dichloroethane to ethylene but this useful product was readily converted into ethane over these catalysts [15–20]. Conversely, group IB-based monometallic Cu or Sn catalysts are effective for the full dechlorination of chlorinated hydrocarbons with higher selectivity toward ethylene; however, such catalysts are less active under mild conditions and can be further deactivated at a relatively high temperature after a long time on stream [21]. For this reaction, bimetallic catalysts such as Pd/Ag, Pt/Cu, Pt/Sn, Pd/Cu and Pd/Ru [14,22–27] have proven to be much more selective toward ethylene than monometallic noble metals.

In this paper, for the first time we report on a catalyst screening for the development of a new sustainable process for the production of trifluoromethyl trifluorovinyl ether by the hydrogen-assisted dechlorination of $CF_3OCFClCF_2Cl$ using activated-carbon-supported metals. Since bimetallic surfaces previously exhibited chemical and catalytic properties very different

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http://dx.doi.org/10.1016/j.apcata.2013.10.038

Table 1
Composition and surface areas of catalysts studied.

Catalyst	Active phase	Composition (% weight)	Surface area (m^2/g)	
			Fresh	Used
0.5-Ru/C	Ru	0.5	920	–
1-Ru/C	Ru	1	1041	795
1.5-Ru/C	Ru	1.5	990	–
1-Ni/C	Ni	1	953	–
2-Ni/C	Ni	2	–	–
1-Pd/C	Pd	1	1074	752
Pd_1-Ru_4/C	Pd and Ru	Pd = 0.8; Ru = 3.2	–	–
Pd_1-Ru_8/C	Pd and Ru	Pd = 0.4; Ru = 3.2	–	–
Pd_1-Cu_2/C	Pd and Cu	Pd = 1; Cu = 1.2	1012	–

from those of the individual systems, the work was concentrated on investigating both monometallic and bimetallic catalysts. These studies led to the development of carbon-supported Pd/Ru and Pd/Cu catalysts which are very active and selective for the studied reaction [28].

2. Experimental

2.1. Catalyst preparation

Ruthenium, nickel, palladium, palladium/ruthenium, and palladium/copper catalysts with different metal content were prepared by the incipient wetness impregnation of a metal precursor solution ($RuCl_3$, $PdCl_2$, $Ni(NO_3)_2$ and $CuCl_2$ supplied by Sigma-Aldrich) on activated carbon (Norit, surface area 1320 m^2/g). Catalysts were dried overnight at 120 °C, then activated with H_2 treatment at 300 °C for 1 h. Due to the nickel higher reduction temperature, Ni-supported catalysts were reduced at 400 °C for 1 h. Table 1 shows the composition and surface area of the materials studied in this work.

2.2. Catalyst characterization

Fresh and used catalysts were characterized by XRD, TEM, TPR, FE-SEM, TGA, and TPD/R/O-MS analysis.

Field emission scanning electron microscopy (FE-SEM) images were observed by a Leo Supra 35 instrument at an acceleration voltage of 20 kV.

XRD measurements were carried out at room temperature with a Bragg/Brentano diffractometer (X'pertPro PANalytical) equipped with a fast X'Celerator detector, using a Cu anode as the X-ray source (Kα, λ = 1.5418 Å). For all the catalysts, the complete diffractogram was collected over the 5–80° 2θ range, counting every 0.1 step for 2 s.

TEM images were acquired by a TEM/STEM FEI Tecnai F20 working at 200 kV. The samples were prepared by dispersion of the powder in ethanol and deposition in a holey-carbon film supported with a titanium grid.

Temperature programmed desorption tests were performed using a Thermoquest TPDRO instrument under He flow or 5%H_2/Ar flow (20 ml/min^{-1}) coupled with MS analysis. The temperature was raised from 60 °C to 500 °C with a heating rate of 10 °C min^{-1}.

Temperature programmed reduction (TPR) analyses were carried out in a Thermo Scientific TPDRO 1100 working with a 5% H_2/Ar reduction mixture. The samples were heated to 700 °C (rate: 10 °C min^{-1}) and kept at this temperature for 30 min.

N_2 adsorption/desorption isotherms (77 K) were performed in a Micromeritics ASAP 2020 instrument. Samples were previously outgassed for 30 min at 150 °C and 30 μmHg, and then heated for 120 min at 250 °C. Specific surface area values were obtained by multi-point BET equation in the 0.01–0.1 p/p0 range.

In order to verify the behavior of fresh and used samples under thermogravimetric analysis, TGA was obtained using a Rheometric Scientific STA1500 analyzer while heating the sample in nitrogen from 25 °C to 680 °C.

2.3. Catalytic activity experiments

The hydrodechlorination of $CF_3OCFClCF_2Cl$ was performed in a 10 mm diameter down-flow Hastelloy® tubular reactor equipped with an internal thermocouple. Liquid $CF_3OCFClCF_2Cl$ was introduced by a perfusion pump, then evaporated in a pre-heated mixer held at 80 °C. Catalytic tests were performed with different contact times (5 and 10 s) and $CF_3OCFClCF_2Cl$ feedings (16% v/v and 33% v/v), with constant $CF_3OCFClCF_2Cl/H_2$ molar ratio equal to 1. Catalytic tests were performed over Ru, Pd, Pd/Ru, and Pd/Cu catalysts at 250 °C, and over Ni catalysts at 300 °C. Each run used approximately 2.72 g of catalyst (20–40 mesh); for bimetallic materials the quantity was adjusted to account for different metal loadings, while keeping constant the ratio between fed AM moles and total metal moles in the catalysts (23 AM/Metals h^{-1}). The gas outlet from the reactor was scrubbed in basic water to collect the HCl formed. The chemical analysis (high-performance wavelength dispersive XRF–Panalytical Axios Advanced Instrument) searching for metals on this solution makes it possible to rule out any metal leaching from catalysts during reaction.

3. Results and discussion

The hydrodechlorination of $CF_3OCFClCF_2Cl$ (AM) in the presence of hydrogen was studied using several heterogeneous metal catalysts supported on activated carbon. The catalytic activity of Ru, Ni, Pd, Pd/Ru, and Pd/Cu materials was investigated at different metal contents. The main product detected during the hydrodechlorination reaction was the target product, $CF_3OCF{=}CF_2$ (MVE). However, Cl/H substitution by-products like $CF_3OCFHCF_2Cl$ and $CF_3OCFClCF_2H$ (AMH), de-fluorinated by-products like $CF_3OCCl{=}CF_2$ (AMH*), and products such as $CF_3OCFHCF_2H$ (AMH_2) were formed in different quantities depending on the catalytic systems used.

Indeed, different possible reaction pathways may be associated with AM hydrodechlorination, as shown in Scheme 1.

To compare the activity performance of various catalysts for the hydrodechlorination reaction, experimental data are summarized in Table 2. Results are expressed in terms of initial $CF_3OCFClCF_2Cl$ conversion, and conversion and different product selectivities after 9 h of time on stream.

3.1. Catalytic activity of Ru-based catalysts

Fig. 1A and B show the activity of Ru-based catalysts with different metal contents. In particular, these figures show the evolution of $CF_3OCFClCF_2Cl$ conversion and MVE selectivity with