Dirhenium complexes supported on silica for the production of highly active single-site heterogeneous catalysts: characterisation of the active sites

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Introduction

Rhenium-based materials are widely used as catalysts in many industrial processes such as metathesis of alkanes, reforming of petroleum feedstocks and selective hydrogenation of organic compounds. Only a few applications of these catalysts in selective oxidations are reported. Recently, several studies have revealed that combinations of rhenium and antimony exhibit activity for the ammoxidation of certain hydrocarbons [1-3]. In particular, bimetallic nanocluster systems based on rhenium combined with antimony or bismuth, highly dispersed on mesoporous silica, are promising catalysts for the ammoxidation of 3-picoline to nicotinonitrile (precursor for niacin) under mild conditions in the liquid phase [4]. These catalysts were produced by supporting organometallic precursor complexes on mesoporous silica. In this contribution, 

Experimental

The three new Re-based nanocluster catalysts (Re₂Sb₂, Re₂Bi₂, and Re₂Sb) were derived from the organometallic precursor complexes: Re₂(CO)_₈(µ-SbPh₂)(µ-H), Re₂(CO)_₈(µ-SbPh₂), and Re₂(CO)_₈(µ-BiPh₂)[5]. These complexes were supported on Davison 911 mesoporous silica FTIR spectra of self-supporting wafers were recorded with a Bruker IFS88 spectrometer. The as-synthesised samples were outgassed up to 400°C in vacuo. CO was adsorbed at room temperature on the activated samples. TGA analysis of the as-synthesised samples was performed on a Setaram SETSYS with a heating rate of 5°C/min up to 600 °C in Ar flow (20 mL/min). Catalysis was performed, after heating to 200°C in vacuo for 2 h the samples, in a Parr pressure reactor, using 5g 3-picoline, 25g toluene, 20bar NH₃, 40bar air, 100mg catalyst and 0.5g tetralin at 423K for 8h (GC internal standard). Product analysis was by GC with FID detector.

Results and discussion

FTIR spectra of the as-synthesized samples outgassed at different pre-treatment temperatures are shown in Fig.1. At room temperature, the Re₂Sb₂, Re₂Bi₂, and Re₂Sb complexes show several bands in the 2110-2000 cm⁻¹ range, due to the stretching modes of the carbonyl ligands. In
particular, the Re\textsubscript{2}Sb complex shows two narrow bands (2105 and 2080 cm\textsuperscript{-1}), whilst the other complexes show only one band (2070 cm\textsuperscript{-1} for Re\textsubscript{2}Sb\textsubscript{2} and 2060 cm\textsuperscript{-1} for Re\textsubscript{2}Bi\textsubscript{2}). These features can be due to the different geometry of Re sites in the complexes. The decomposition of the organometallic complexes, as observed by the disappearance of the bands in the C-O stretching (2000-2105 cm\textsuperscript{-1}) and C-C, C-H bending (1600-1400 cm\textsuperscript{-1}) ranges, occurred at different temperatures. Further evidence for the thermal decomposition of the ligands is obtained from the TGA analysis. CO adsorption on the activated samples was performed to clarify the nature of the catalytic sites. In the case of Re\textsubscript{2}Sb\textsubscript{2} and Re\textsubscript{2}Bi\textsubscript{2}, weak bands (2062, 2052 cm\textsuperscript{-1} and 2052 cm\textsuperscript{-1}, respectively), assigned to the stretching mode of CO adsorbed on Re\textsuperscript{0} centres, are formed. In the case of Re\textsubscript{2}Bi\textsubscript{2} the band is quite symmetric, indicating the presence of well defined single-site Re\textsuperscript{0} exposed at the surface of the metal nanoparticles. On the contrary, in the Re\textsubscript{2}Sb sample, a band at 2130 cm\textsuperscript{-1} is also formed and is assigned to CO adsorbed on partially reduced Re\textsuperscript{ni+} sites, which indicates the presence of Re in higher oxidation states [6]. In catalytic testing for the ammoxidation of 3-picoline to nicotinonitrile, the molar conversion increased in the order Re\textsubscript{2}Sb (37%) < Re\textsubscript{2}Sb\textsubscript{2} (42%) < Re\textsubscript{2}Bi\textsubscript{2} (65%), with all three having similar selectivities to nicotinonitrile (75-78%). A pure Re sample, prepared in similar fashion, gave a conversion of 12% [4]. These results indicate that while both bismuth and antimony can be used as modifiers for this type of catalyst, bismuth gives superior performance in the ammoxidation of 3-picoline. The improved activity of Re\textsubscript{2}Sb\textsubscript{2} against Re\textsubscript{2}Sb indicates that a higher proportion of Re\textsuperscript{0} centres is beneficial for this reaction.

Conclusions
The spectroscopic data are in agreement with the catalytic trend and indicate that single Re\textsuperscript{0} centres are required for high catalytic performance.

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References