Journal of Catalysis 278 (2011) 228–238

Contents lists available at ScienceDirect

Journal of Catalysis

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

Selective hydrogenation of amides using bimetallic Ru/Re and Rh/Re catalysts

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ARTICLE INFO

Article history:
Received 2 November 2010
Revised 14 December 2010
Accepted 15 December 2010
Available online 26 January 2011

Keywords:
Heterogeneous catalysis
Ruthenium
Rhenium
Rhodium
Bimetallic
Hydrogenation
Amide
Primary amine
Characterization
Reaction mechanism

ABSTRACT

Heterogeneous Ru/Re and Rh/Re catalysts, formed in situ from $Ru_3(CO)_{12}$/$Re_2(CO)_{10}$ and $Rh_6(CO)_{16}$/$Re_2(CO)_{10}$ respectively, are effective for the liquid phase hydrogenation of cyclohexanecarboxamide ($CyCONH_2$) to $CyCH_2NH_2$ in up to 95% selectivity without the requirement for ammonia to inhibit secondary and tertiary amine formation. Good amide conversions are noted within the reaction condition regimes 50–100 bar H_2 and $\geqslant$150 (Rh) – 160 °C (Ru). Variations in Ru:Re and Rh:Re composition result in only minor changes in product selectivity with no evidence of catalyst deactivation at higher levels of Re. In situ HP-FTIR spectroscopy has shown that catalyst genesis occurs via decomposition of the metal carbonyl precursors. Ex situ characterization, using XRD, XPS and EDX-STEM, has provided evidence for the active components of these catalysts containing bimetallic Ru/Re and Rh/Re nanoclusters, the surfaces of which become significantly oxidized after use in amide reduction. Potential mechanistic pathways for amide hydrogenation are discussed, including initial dehydration to nitrile, a pathway potentially specifically accessible to primary amides, and evidence for often postulated imine intermediates.

1. Introduction

The generation, characterization and use of bimetallic heterogeneous Rh/Mo and Ru/Mo catalysts for the selective hydrogenation of amides to amines in the liquid phase has recently been described [1,2]. Key features of this work include both high catalyst selectivity for the reduction of primary amides to the respective primary amines, without the necessity for the addition of ammonia and/or amines to inhibit side reactions leading to secondary and tertiary amine by-products, and considerably milder reaction conditions relative to those required by standard first generation copper chromite catalysts [3]. Catalyst performance was shown to be crucially dependent on Mo:Rh and Mo:Ru composition, respective ratios of >2 and >1 leading to either significant, or complete, inhibition of catalysis.

Rhenium-based catalysts have received greater attention than Rh, Ru or Mo for the reduction of 'difficult' functional groups such as amides, and particularly carboxylic acids and esters. Broadbent et al. [4] described the use of Re_2O_7 as a catalyst precursor for the hydrogenation of carboxylic acids under the severe reaction conditions (312 bar H_2, 217 °C, 6 h) typically required by copper chromite catalysts. A step change was described in 1990 by Yoshino et al. [5] with a report of the use of promoted bimetallic Re/Os catalysts under considerably milder reaction conditions (25–100 bar H_2, 100–120 °C, 6 h), with highest alcohol selectivities being favoured at the highest pressure. A subsequent very recent development is the use of titania-supported Pt (and Pt/Re) catalysts with optimum reaction conditions at 20 bar H_2 and 130 °C, although very low reaction rates at as low as 5 bar H_2 and 60 °C are also quoted [6]. The first account of the use of Re in amide reduction was also provided by Broadbent et al. [7], who described the use of Re(VI) oxide for the selective hydrogenation of benzamide to benzylamine (205 bar H_2, 220 °C, 49 h, ethanol solvent) in 69% yield, with toluene as the only by-product. Surprisingly, the formation of neither cyclohexylamine nor N-ethyl-substituted secondary or tertiary amine derivatives were reported [cf. Ref. [2]]. Subsequently, a BP patent claimed the use of a Pd/Re/high surface area graphite/zeolite 4A combination, dispersed in a solvent such as 1,4-dioxane, for the reduction of amides at 130 bar H_2 and 200 °C [8]. Using propionamide as substrate, the product distribution comprised a mixture of primary, secondary and tertiary amines. Fuchikami et al. [9] briefly described the behaviour of Rh/Re catalysts for the reduction of a range of amides. In the one example of a primary amide tested, *n*-hexanamide required the co-addition of an amine (diethylamine) to induce good selectivity to *n*-hexylamine under reaction conditions of 100 bar H_2 and 180 °C. Otherwise di(*n*-hexyl)amine comprised the predominant

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doi:10.1016/j.jcat.2010.12.009

product, in complete contrast to our recent findings with Rh/Mo and Ru/Mo catalysts using cyclohexanecarboxamide ($CyCONH_2$) as substrate [1,2]. Here, the genesis and performance of both Ru/Re and Rh/Re catalysts in the hydrogenation of $CyCONH_2$ (and *N*-acetylpiperidine) are reported, together with ex situ characterization using microanalysis, XRD, XPS and EDX-STEM.

2. Materials and methods

With the exception of the additional details described below, experimental and analytical procedures are as outlined in Refs. [1,2].

2.1. Reagents

$Re_2(CO)_{10}$ (98%) was purchased from Strem Chemicals and the XPS standard, Re foil (0.025 mm thickness, 99.98%), from Aldrich Chemicals.

2.2. Catalytic procedures

A typical 'single-pot' batch Ru/Re catalyst preparation, and evaluation in $CyCONH_2$ reduction, was carried out as follows, for a nominal Re:Ru atomic composition of 0.25. $[Ru_3(CO)_{12}]$ (22 mg, 0.103 mmol Ru), $[Re_2(CO)_{10}]$ (8.4 mg, 0.026 mmol Re) and cyclohexanecarboxamide (0.235 g, 1.85 mmol) contained in a glass liner were dissolved in 1,2-dimethoxyethane (DME) (30 mL) and *n*-octane (0.100 g) added as an internal standard for GC analysis. The liner was placed in a ca. 300-mL capacity pressure vessel and the reaction mixture, under agitation, purged three times with N_2 (at 5 bar), and three times with H_2 (5 bar). The autoclave was then pressurized to 100 bar H_2 and heated to 160 °C for 16 h. A very dark coloured liquid was initially recovered after cooling and venting and from this a black residue slowly settled, leaving a colourless solution. The residue was separated by centrifugation (2000 rpm, 20 min) and the supernatant liquid containing reaction products removed. After several washings with DME (10 mL), the catalyst residue (ca 15 mg) was dried and the resultant fine black powder either recycled using the same quantities of fresh substrate and solvent, or characterized using the techniques described below. Product solutions were analysed by GC as previously described [1].

In addition to 'batch' experiments, 'parallel' catalyst evaluations were also conducted. A typical 'parallel' catalyst evaluation was carried out using the standard autoclave used for batch runs, modified to accommodate four vertically mounted modified test tubes of ca. 20 mL capacity, all containing mini-magnetic followers to ensure effective stirring. Using a 10 mL volume of DME solvent, the scale of substrate and catalyst precursors (4 mol% Ru) were reduced accordingly.

2.3. Ex situ characterization

2.3.1. EDX-STEM

Sample quantification was determined using the most intense 'pure' Ru K 1α (19.279 keV) and Re L 1α (8.654 keV) lines that are largely free from interference by signals from other elements. Even so, both trace O and Si were also detected during the analysis and deconvolution of the Si K and Re L lines became necessary for accurate quantification. Also, since Ru K and Re L lines are under comparison, the quoted values are subject to an error of ±5%.

2.3.2. Microanalyses

All elemental analyses were performed by Mr. S.G. Apter, Department of Chemistry, University of Liverpool. Transition metal concentrations were determined using a Spectro Ciros CCD Inductively Coupled Plasma (ICP) source linked to Atomic Emission Spectroscopy (AES). Sample digestion was accomplished using a matrix combination containing aqua regia (2 eq. HCl: 1 eq. HNO_3) (5 mL) and HF (0.5 mL), followed by microwave treatment in a CEM MARS5 oven using the following programme conditions; heating to 220 °C at 20 °C min^{-1}, holding at 220 °C for 20 min followed by a cooling period of 20 min. The resultant solutions were diluted to 100 mL in distilled water and referenced against Ru, Rh and Re standards made up in similar $HCl/HNO_3/HF$ matrix solutions. Application of this procedure overcame the well-known resistance of Ru in particular to digestion [10] (see Supplementary material S2 for further details).

Standard C, H and N determinations were carried out by combustion analysis using either a Flash EA-1112 or a Model 1106 Carlo Erba thermal elemental analyzer at ~2000 °C. For the bimetallic catalyst samples, a V_2O_5 catalyst was required to aid combustion.

3. Results and discussion

3.1. N-acetylpiperidine hydrogenation using Ru/Re catalysts

A hydrogenation catalyst derived from $Ru_3(CO)_{12}$ and $Re_2(CO)_{10}$ (Re:Ru = 1.0, 1 mol% Ru) was reported by Fuchikami et al. [9] to give high conversions of *N*-acetylpiperidine into *N*-ethylpiperidine (96% yield) under standard reaction conditions of 100 bar H_2 and 160 °C. Ru alone was essentially inactive (1% conversion and amine yield) and Re showed low activity (14% conversion) with only 7% yield of the desired amine. Repetition of this work using $Re_2(CO)_{10}$ has confirmed reproducibility (16% conversion, 53% amine selectivity) and revealed that competing C—N bond hydrogenolysis of *N*-acetylpiperidine (to ethanol and piperidine) accounts for the additional products. No attempts to use Ru/Re catalysts for the reduction of primary amides such as cyclohexanecarboxamide, $CyCONH_2$, have been reported and this has provided the focus for our work.

3.2. $CyCONH_2$ hydrogenation using Ru/Re catalysts

3.2.1. Variation of Re:Ru composition

Using a series of parallel experiments (10 mL scale and 4 mol% catalyst, based on Ru), the results of variation in Re:Ru ratio are shown in Fig. 1. From this, it is evident that the addition of only a small concentration of $Re_2(CO)_{10}$ to $Ru_3(CO)_{12}$, comparable to that observed with Ru/Mo (and Rh/Mo) catalysts, is necessary to initiate analogous overall conversion/product selectivity synergy. In contrast however there is no evidence of significant reduction in conversion with increasing Re content, for up to Re:Ru = 1.8. Moreover, product selectivity remains essentially constant between Re:Ru values of 0.25 and 1.1, with uniformly trace amounts of $(CyCH_2)_2NH$ present across the range Re:Ru = 0.3–1.8, and only at Re:Ru = 1.8 are slight divergences of product distribution in favour of $CyCH_2OH$ apparent. A Re:Ru composition of ca. 0.3 appears optimum for a combination of conversion and selective formation of $CyCH_2NH_2$ (both >90%). The conversion and selectivity recorded for the Re:Ru = 0.34 catalyst in Fig. 1 are those obtained from the final reaction solution from the in situ HP-FTIR experiment using the complete $CyCONH_2$ reduction system, described in Section 3.6.1, thus confirming internal consistency between the two sets of experimental data.

Furthermore, for the purposes of checking reproducibility between 'parallel' and 'batch' processing, three Ru/Re catalysts were examined in batch experiments, using 5 mol% Ru. The results summarized in Table 1 provide confirmation, with essentially the same reaction product profile and only a marginal improvement in