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Selective hydrogenation of amides using Rh/Mo catalysts

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ABSTRACT

Rh/Mo catalysts formed in situ from $Rh_6(CO)_{16}$ and $Mo(CO)_6$ are effective for the liquid phase hydrogenation of $CyCONH_2$ to $CyCH_2NH_2$ in up to 87% selectivity, without the requirement for ammonia to inhibit secondary amine formation. Use of in situ HP-FTIR spectroscopy has shown that decomposition of metal carbonyl precursors occurs during an extended induction period, with the generation of recyclable, heterogeneous, bimetallic catalysts. Variations in Mo:Rh content have revealed significant synergistic effects on catalysis, with optimum performance at values of ca. 0.6, and substantially reduced selectivities at $\geqslant 1$. Good amide conversions are noted within the reaction condition regimes 50–100 bar H_2 and 130–160 °C. Ex situ characterization of the catalysts, using XRD, XPS and EDX-STEM, has provided evidence for intimately mixed (ca. 2–4 nm) particles that contain metallic Rh and reduced Mo oxides, together with MoO_3. Silica-supported Rh/Mo analogues, although active, perform poorly at <150 °C and deactivate during recycle.

1. Introduction

The discovery and development of methods for the selective catalytic reduction of ‘difficult’ functional groups such as amides, carboxylic acids and esters have been recognised for many years as a formidable problem [1], within which grouping amides are acknowledged to represent the most extreme difficulty. Traditional copper chromite-based catalysts, either alone [2] or dispersed in zeolites [3], require both severe reaction conditions, e.g. 200–350 bar H_2 and 250–400 °C, and high catalyst loadings (ca. 20 wt%).

The concept of ‘bimetallic’ catalysis, in which the presence of two different elemental components leads to synergistic behaviour, is relevant to developments in this area. A 1988 BP patent claims the use of a Pd/Re/high surface area graphite/zeolite 4A combination, dispersed in a solvent such as dioxane, for the reduction of amides at 130 bar H_2 and 200 °C [4]. More recently a series of ‘bimetallic’ catalysts (particularly Rh/Mo and Rh/Re), based largely on the respective metal carbonyls as precursors [5–7], have been described for the hydrogenation of amides and carboxylic acids under conditions (typically 100 bar H_2, 160–200 °C) that are considerably milder than those required by copper chromite. No characterization data have been described for any of these emerging catalyst systems, and they have even been referred to as homogeneous catalysts, notwithstanding the reaction conditions used.

The simple stoichiometry for the reduction of an amide (Eq. (1)) to the corresponding amine requires two equivalents of molecular hydrogen, one of which

$$RC(O)NR'R'' + 2H_2 \rightarrow RCH_2NR'R'' + H_2O \qquad (1)$$

serves for the elimination of the carbonyl oxygen as water. Thus the commonly used term ‘hydrogenation’ is not totally representative of the processes involved. In previous work the reduction of tertiary amides, in particular of *N*-acetylpiperidine (NAP) to *N*-ethylpiperidine (NEP), was described [6].

The selective reduction of a primary amide to the corresponding primary amine is not only of considerably greater potential importance, but also represents a greater challenge than tertiary amides, because of the higher probability of the occurrence of side reactions leading, in particular, to the co-formation of undesired secondary and tertiary amines (Scheme 1), as exemplified by the reduction of propionamide to a mixture of primary, secondary and tertiary amine products [4]. This problem is also manifest in chemistry associated with the catalytic hydrogenation of nitrile functional groups [8], both of which are postulated to involve reactive imine intermediates. It is well-established that co-addition of ammonia, also amines [8,9], effectively inhibits undesirable amine-imine coupling reactions that lead to the formation of secondary

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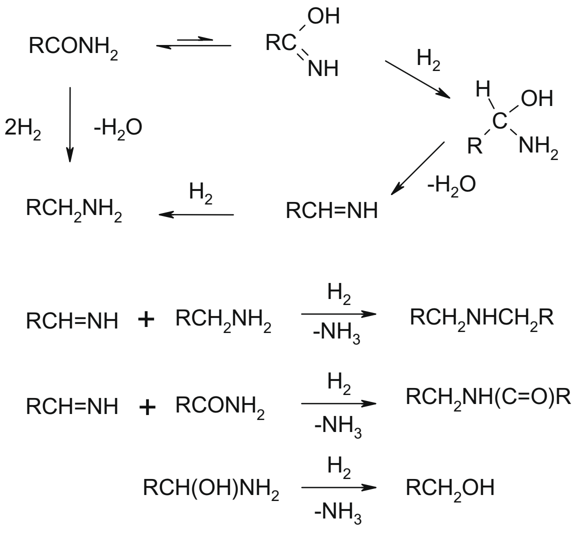

Scheme 1. Primary amide hydrogenation: reaction pathways to by-products, highlighting the significance of the postulated imine intermediate. All transformations are assumed to occur via substrate adsorption at the Rh/Mo surfaces.

and tertiary amines, a feature that has been very clearly re-emphasized as a mandatory requirement in a recent report of a homogeneous Ru/triphos-based catalyst for amide hydrogenation [10]. The addition of ammonia and amines usually incurs a reaction rate penalty, moreover their presence leads to complications in both product separation and catalyst recovery; methods of achieving high primary amine selectivities in the absence of such reagents are therefore highly desirable.

The work described here concerns the genesis, characterization and use of a range of Rh/Mo catalysts prepared according to [6], which indeed do not require the addition of ammonia or amines to inhibit secondary amine formation. This finding is exemplified in detail by the selective hydrogenation of cyclohexanecarboxamide, $CyCONH_2$, a convenient representative example of a primary amide functional group, to cyclohexanemethylamine, $CyCH_2NH_2$. These catalysts have been described as ‘Rh/Mo’ because the intrinsically active catalyst centre is rhodium. Where however reference has been made to variations in Rh/Mo content, different amounts of Mo have been added to a fixed concentration of Rh, and in these sections the reciprocal terminology Mo:Rh has been used to emphasize the very significant effects resulting from the addition of small quantities of Mo to poorly performing Rh catalysts.

2. Materials and methods

2.1. Reagents

$Mo(CO)_6$ was supplied by Alfa Organics, $RhCl_3{\cdot}3H_2O$ (99.9%) by Strem, cyclohexanecarboxamide (97%), cyclohexanemethylamine, *n*-butyramide, *n*-butylamine and $LiOH{\cdot}H_2O$ (98%) by Aldrich Chemicals, benzamide by Fisons, Mo_2C, $[Rh(CO)_2(acac)]$ and Rh_2O_3 by Johnson Matthey, Rh (1 wt%) on Graphimet by Rhone-Poulenc, $CuCr_2O_4$ by Separation Ltd., 1, 2-dimethoxyethane (DME) and MoO_3 (Analytical grade) by BDH and H_2 (>99.995%), N_2 and CO gases by BOC.

2.1.1. N-Acetylpiperidine (NAP)

N-Acetylpiperidine (NAP) was prepared in a quantitative yield by acetylation of piperidine using acetic anhydride (see Supplementary material S1).

2.1.2. Methylcyclohexanecarboxamide ($CyCONHCH_3$)

Methylcyclohexanecarboxamide ($CyCONHCH_3$), white crystals, was prepared in 90% yield by hydrogenation of its phenyl analogue over Pd/C (0.5 mol%) at 160 °C for 16 h. Expected for $C_8H_{15}NO$ (C 68.04, H 10.71, N 9.92), Found (C 67.69, H 10.65, N 9.81); m. pt. 111–114 °C; 200 MHz ^1H–NMR ($CDCl_3$), δ 1.23–1.81 (m, 11), 2.78 (d, 3), 6.51 (br, 1); CI–MS *m*/*z* 142 $[M]^+$, 156 $[M + NH_4]^+$.

2.1.3. Rh_6 $(CO)_{16}$

Rh_6 $(CO)_{16}$ was prepared using a modified literature procedure [11] (See Supplementary material S1).

2.2. Preparation of supported catalysts

2.2.1. Rh/MoO_3 catalyst via co-precipitation

Solutions of $RhCl_3{\cdot}3H_2O$ (0.119 g, 0.45 mmol) in water (20 mL), and ammonium paramolybdate, obtained from MoO_3 (1.0 g, 6.95 mmol) dissolved in 30% aqueous ammonia (3 mL), were carefully mixed and slowly evaporated to dryness to give a green solid (ca. 1.0 g). This was heated to 150 °C, leading to the elimination of NH_4Cl, and then to 300 °C to generate the mixed oxides. Activation by reduction in hydrogen was effected immediately prior to use in catalyst testing.

2.2.2. Silica-supported catalysts, nominally 10 wt% Rh/Mo ex-metal carbonyls, on Cab-O-Sil 300

Both (i) single- and (ii) two-stage preparative methods were employed. (i) Cab-O-Sil 300 (1.00 g), $Mo(CO)_6$ (0.275 g), $Rh_6(CO)_{16}$ (0.083 g) in DME (20 mL) were treated, with constant stirring, under hydrogen, at 100 bar and 160 °C, for 16 h. After cooling and depressurizing the black product was filtered, washed with DME, and dried in air. Elemental composition Rh 6.83, Mo 7.27, C 4.10, H 0.80, Si 44.20%, Mo:Rh = 1.06. (ii) The two-stage process involved sequential treatments of silica, first with $Mo(CO)_6$ (0.275 g), under the above-mentioned reaction conditions yielding a brown-grey powder which turned dark blue on exposure to air. $Rh_6(CO)_{16}$ (0.083 g) was added to a dispersion of a portion (0.5 g) of this solid in DME, and the high pressure, high temperature hydrogen treatment repeated. A similar black product, more homogeneous in appearance than that isolated from the single stage preparation, was obtained. Elemental composition Rh 8.11, Mo 5.61, C 3.47, H 0.77, Si 43.28%, Mo:Rh = 0.69.

2.3. Catalytic procedures

Preliminary experiments using NAP were performed at a Rh concentration of 1 mol% as described by Fuchikami et al. [6]. For the reduction of primary amides such as $CyCONH_2$, a typical catalyst preparation was carried out as follows, for the ‘one-pot’ genesis and evaluation of a Rh/Mo catalyst containing a Mo:Rh atomic ratio of 0.55. $Rh_6(CO)_{16}$ (0.0165 g, 0.0930 mmol Rh), $Mo(CO)_6$ (0.0135 g, 0.0511 mmol Mo) and $CyCONH_2$ (0.235 g, 1.85 mmol) were added to a glass liner containing DME (30 mL), and *n*-octane (0.100 g) 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, was purged (at 5 bar), 3 times with N_2 followed by 3 times with H_2. The autoclave was then pressurized to 100 bar with H_2 and heated to 160 °C for 16 h. After cooling and depressurization, a dark coloured colloidal suspension was recovered. This slowly settled to leave a colourless solution, and dark residue (ca. 15 mg), which was separated by centrifugation (2000 rpm, 20 min), washed several times with DME and dried as a fine black powder.

The above-mentioned procedure was adopted for all ‘one-pot’ reactions. In the experiment involving the effect of LiOH on prod-