Synthesis of Primary Amines with OMS-2

**Significance:** Manganese oxide based octahedral molecular sieves (OMS-2) catalyzed the reaction of primary alcohols with aqueous ammonia to give the corresponding amides in 65–99% yield under molecular oxygen (10 examples, eq. 1). The reactions of aldehydes and nitriles with aqueous ammonia also proceeded in the presence of OMS-2 to give the corresponding amides in 77–98% yield (16 examples, eq. 2). In the formation of 2-pyridinecarboxamide from 2-pyridinemethanol, the catalyst was recovered by filtration and reused eleven times without significant loss of its catalytic activity (1st reuse: 93% yield, 11th reuse: 85% yield).

**Comment:** Suib and co-workers have previously reported the preparation of OMS-2 (Chem. Mater. 1994, 6, 815). In the formation of benzamide from benzyl alcohol, the catalytic activity of OMS-2 was superior to that of precursors of OMS-2 (KMnO₄, MnSO₄·H₂O), other manganese-based oxides (MnO₂ and Mn₃O₄) and other metal oxides (Co₃O₄, CeO₂). After the reaction of benzyl alcohol with aqueous ammonia, no leaching of manganese species was observed by ICP-AES analysis.

**Results:**

OMS-2 (100–200 mg, Mn component: 27–54 mol%) in 1,4-dioxane, 130 °C under O₂ (3 atm) gave the corresponding amides in 45–97% yield.

**Selected examples:**

1. **Synthesis of animes from primary alcohols:**
   - R-OH + aq NH₃ (0.5 mmol) → R-NH₂ (ca. 2.6 equiv)
   - NH₂

2. **Syntheses of animes from aldehydes and nitriles:**
   - R-X + aq NH₃ (0.5 mmol) → R-NH₂ (ca. 2.6 equiv)

3. **Selected examples:**
   - 3 h, 96% yield (X = CHO)
   - 3 h, 97% yield (X = CN)
   - 3 h, 95% yield (X = CHO)
   - 3 h, 99% yield (X = CN)
   - 3 h, 87% yield (X = CHO)
   - 3 h, 87% yield (X = CN)
   - 3 h, 93% yield (X = CHO)
   - 3 h, 93% yield (X = CN)
   - 1 h, 95% yield (X = CHO)
   - 1 h, 96% yield (X = CN)
   - 24 h, 65% yield (X = CHO)
   - 24 h, 98% yield (X = CN)
   - 1 h, 94% yield (X = CHO)
   - 1 h, 96% yield (X = CN)
   - 24 h, 77% yield (X = CHO)
   - 24 h, 98% yield (X = CN)

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