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.

**Synthesis of amides from primary alcohols:**

\[
R-OH \quad + \quad aq \ NH_3 \quad \xrightarrow{1,4\text{-dioxane, } 130^\circ C, \ O_2 (3 \ atm)} \quad NH_2-R \quad \xrightarrow{21 \ examples, \ 45-97\% \ yield}
\]

**Results:**
- 3 h, 96% yield
- 3 h, 97% yield
- 3 h, 95% yield
- 3 h, 99% yield

**Syntheses of amides from aldehydes and nitriles:**

\[
R-X \quad + \quad aq \ NH_3 \quad \xrightarrow{1,4\text{-dioxane, } 130^\circ C, \ O_2 (3 \ atm, \ X = \text{CHO})} \quad NH_2-R \quad \xrightarrow{16 \ examples, \ 77-98\% \ yield}
\]

**Selected examples:**
- 3 h, 89% yield (X = CHO)
- 3 h, 91% yield (X = CN)
- 3 h, 87% yield (X = CHO)
- 3 h, 93% 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)

**OMS-2 (100–200 mg, Mn component: 27–54 mol%)**