

Towards nitrogen analogues of Mars-van Krevelen processes?

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Introduction

In recent years, spurred by the accessibility of high surface area forms prepared by ammonolysis, the application of metal nitrides and oxynitrides as catalysts has attracted great interest^{1,2,3}. Much of this interest has been concentrated in two distinct areas – the analogous behaviour of some early transition metal nitrides and precious metals in catalytic reactions, and the modified basicity imparted in incomplete nitridation of metal oxides. In the former case, fairly extensive investigation of reactions involving hydrogen transfer such as hydrogenation and hydrotreating have been made, whilst in the latter case oxynitrides have been applied to transformations such as Knoevenagel reactions. In addition to these applications, some limited interest has also centred upon the use of various nitrides as catalyst supports, where arguments of beneficial behaviour have been advanced in terms of lack of reactivity and/or superior thermal conductivity.

To date, the potential ability of metal nitrides to act as nitrogen transfer agents in catalytic processes involving mechanisms analogous to the well-known Mars-van Krevelen process in metal oxides seems to be largely overlooked. This is despite early reports of its possible occurrence⁴. Very recently, Mars-van Krevelen type nitrogen transfer processes have been reported in some propane ammoxidation catalysts⁵. The Mars-van Krevelen oxidation mechanism is essentially that in which the lattice oxygen of oxide catalysts is the active oxidant, with the vacancies so formed being replenished in a separate reaction event. In this presentation, we give a comprehensive description of our very recent results in the area of nitrogen transfer from the lattice of nitrides. Our studies have centred upon comparisons of ammonia synthesis rates both in the presence and absence of gas-phase nitrogen with a range of different transition metal nitride systems including the various different polymorphs of molybdenum nitride and Co₃Mo₃N.

Materials and Methods

A variety of molybdenum nitride materials have been prepared according to standard literature methods and phase determinations have been performed by power x-ray diffraction using a Siemens D5000 diffractometer. Catalytic testing has been performed in a fixed bed quartz microreactor. Catalysts were re-nitrided at 700°C under a 75 vol% H₂ - 25% vol % N₂ mixture for 2h prior to the determination of steady state ammonia synthesis reaction rates under the same gas mixture at 400°C. For comparison, to gauge the relative rates of reaction of “lattice” nitrogen, the same activation procedure has been employed but, upon reaction, the nitriding mixture has been replaced with 75 vol % H₂ – 25 vol % Ar. The effect

of elevated temperature upon both reaction rate and phase composition have also been investigated.

Results

The mass normalised steady state ammonia synthesis activity for a selection of the molybdenum based materials to be discussed are presented in Table 1. Materials initially loaded as oxides were nitrided by the activation procedure resulting in β-Mo₂N in the case of MoO₃ and Co₃Mo₃N in the case of CoMoO₄.nH₂O. Data have also been determined for reaction with H₂/Ar and generally it is found that the extent of ammonia synthesis is rather limited although not negligible. This will be quantified in the talk and explored in terms of the extent to which a Mars – van Krevelen type process can occur under various reaction conditions. In the case of Co₃Mo₃N, the lattice parameters are found to significantly change upon reaction under this regime at elevated temperature and this observation, in conjunction with the reactivity data, will be critically explored in relation to the overall objectives of the study.

precursor material	steady state ammonia synthesis rate/ μmol g ⁻¹ h ⁻¹
MoO ₃	24.5
γ-Mo ₂ N	34.3
CoMoO ₄ .nH ₂ O	134.2
Co ₃ Mo ₃ N	167.2
δ-MoN	3.8

Significance

This work will fundamentally address the possibility of the occurrence of nitrogen analogues of Mars-van Krevelen processes in nitride catalysts. This possibility is of widespread potential application and may offer opportunities for new strategies in nitrogen transfer catalysis leading to, for example, new routes to aniline synthesis. It can be envisaged that such strategies may involve two stage type processes wherein catalysts are “loaded” with nitrogen under one reaction regime and reactive forms of such nitrogen are released under a different regime.

References

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