

A Novel Calcination Method for Supported Metal Nitrate Catalyst Precursors

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ABSTRACT

The preparation of nickel and cobalt on silica catalysts by impregnation and drying using aqueous metal nitrate solutions was studied in detail. Using ordered mesoporous silica (SBA-15) as a model support, we investigated the effects of impregnation, drying and calcination on the final dispersion. Extensive agglomeration of dried precursor-species during calcination in air was demonstrated. Calcination using a gas flow containing a low concentration of NO, restricted this mobility and enabled the preparation of highly loaded (15-24 wt%) and well-dispersed nickel oxide (3-4 nm) and cobalt oxide (4-5 nm) silica catalysts. After reduction a thus calcined cobalt oxide on silica catalyst showed a high activity in the Fischer-Tropsch synthesis.

1. INTRODUCTION

Impregnation and drying is an important technique for the preparation of supported heterogeneous catalysts. The nature of the precursor salt has a large impact on the ultimate dispersion of the active phase. It is for example well-known that metal nitrates (highly water soluble, low costs) as precursors for cobalt and nickel catalysts generally yields poorly-dispersed catalysts. Until now, the reason for this is not well understood. Fundamental studies have been hampered by the heterogeneity of conventional supports like silica gel, which makes it difficult to disentangle the effects of the individual preparation steps (impregnation, drying, calcination and reduction) on the ultimate metal dispersion. In this respect, the family of ordered mesoporous materials provides ideal model systems. The well-defined pore size and geometry of these supports facilitate the use of advanced characterization techniques such as electron tomography (3D-TEM) and more conventional bulk techniques as N₂-physisorption and XRD. We used SBA-15 as model support to investigate the effect of the individual preparation steps on the ultimate nickel and cobalt dispersion using nitrates as precursor salts.

2. EXPERIMENTAL

SBA-15 was prepared according to a literature procedure [1] and silica gel was used as received from Grace-Davison. These supports were impregnated to incipient wetness with aqueous metal nitrate solutions to provide 15 or 18 wt% cobalt and 20 or 24 wt% nickel on SBA-15 or silica gel, respectively. The samples were dried in air by heating from room temperature (RT) till 120 °C and kept at this temperature for 12 hours. Calcination in a flow of air or of 1 vol% NO/He was carried out in a fixed bed reactor by heating from RT to 450 °C with 1 °C.min⁻¹. The reduction step was carried out by heating the samples till 500 °C in a flow of argon containing 5 vol% H₂.

3. RESULTS AND DISCUSSION

XRD and TEM (Fig. 1a) results for SBA-15 demonstrated that during drying no large agglomerates of nitrate precursor had formed. After calcination in air severe redistribution had taken place, resulting in nickel oxide particles blocking the mesopores, and large particles (8-60 nm) situated at the exterior of the support particles. (Fig. 1b). Following identification of calcination as the most detrimental step we focussed on the effect of the calcination conditions on the degree of redistribution. We found that the composition of the gas flow largely affected the ultimate metal oxide particle sizes.

Figure 1: TEM images of SBA15 after impregnation and drying with nickel nitrate (a) after air calcination (b) and after NO calcination (c).

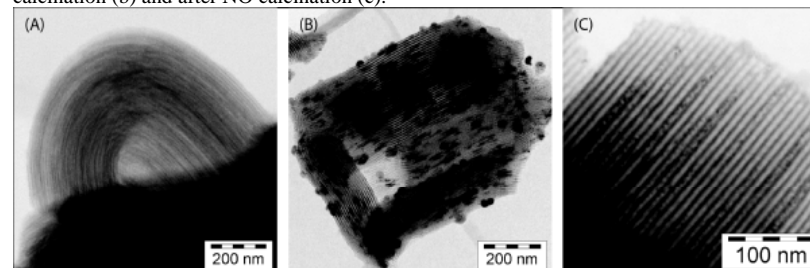


Figure 1: TEM images of SBA15 after impregnation and drying with nickel nitrate (A) after air calcination (B) and after NO calcination (C).

Following these systematic investigations, we developed a novel calcination treatment using 1 vol% NO in an inert gas that led to highly dispersed cobalt and nickel oxide (Fig. 1c). The obtained particle sizes for the individual preparation steps of the nickel catalysts are shown in Table 1. Experiments with conventional silica gel showed similar results. *In situ* XRD results demonstrated that the role of NO is related to its moderating effect on the rate of nitrate decomposition. Catalytic tests after reduction of the cobalt oxide on silica gel catalyst demonstrated that a highly active Fischer-Tropsch catalyst with a cobalt time yield of 3.6×10^{-5} mol_{CO}/(g_{Co}·s) was obtained at 220 °C, 1 bar, H₂/CO=2 v/v and 2 % CO conversion.

Table 1: Nickel phase particle sizes after individual preparation steps

Support	Dried d _{XRD} (nm)	Calcination Treatment	Calcined d _{XRD} (nm)	Calcined d _{TEM} (nm)	Reduced d _{XRD} (nm)	Reduced d _{TEM} (nm)
SBA-15	9	Air	10	8-60	12	10-40
SBA-15	9	NO	4	3-4	4	4-5
Silica gel	12	Air	15	14-90	16	15-70
Silica gel	12	NO	4	4-5	4	4-5

Reference

Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G.H.; Chmelka, B.F. and Stucky, G.D. (1998) *Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores*. Science **279** 548-552