Preparation of supported nickel oxide with tunable particle size via confinement

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Introduction

Supported metal (oxide) catalysts are essential for the production of fuels and chemicals as well as the reduction of environmental pollution. Control over the size distribution is key to the efficient use of metal (oxide) nanoparticles. An example is the dependence of the Fischer-Tropsch synthesis activity on cobalt particle size, where an optimum in activity was found for 6 nm Co particles [1]. Ordered mesoporous supports with varying pore diameters have been applied to influence the cobalt particle size using nitrate precursors [2]. However, especially for higher loadings, the use of metal nitrate precursors results in a low dispersion after calcination, due to agglomeration and migration to the external surface [3]. Recently it was shown that replacement of the air calcination by a 1%v/v NO/He thermal treatment, prevents this agglomeration, resulting in highly dispersed supported cobalt and nickel oxides at high loadings [4]. In this contribution we will show that the nickel oxide particle size can be tuned by combining the confinement effect of mesoporous supports with controlled decomposition under NO.

Materials and Methods

SBA-15 was prepared according to literature [5]. Materials with different pore diameters were obtained by aging at 80°C (pore diameter (PD) = 9.7 nm) and 60°C (PD = 8.3). Pore diameters were determined by N_2-physisorption using an NL-DFT method. MCM-41 was synthesized according to the procedure reported by Cheng et al. [6]. Materials with three different pore diameters were synthesized by variation of the template; $C_{19}H_{42}NBr$ (PD = 3.7 nm), $C_{13}H_{30}NBr$ (PD = 2.5 nm) and $C_{17}H_{38}NBr$ (PD = 4.6 nm). The aging temperature was 100°C for the first two templates and 150°C for the latter. All samples were impregnated to incipient wetness with a 4.3 M aqueous nickel nitrate solution, followed by drying at 120°C for 12 hours. After impregnation and drying the samples were calcined at 350°C for 2 hours (5°C/min) in either a flow of air or 1% v/v NO/Ar. The NiO loading of the catalysts was in the range 16-22 wt%, depending on the pore volume. XRD measurements were performed with a Bruker-AXS D8 diffractometer equipped with a $CoK_{\alpha1,2}$ source. The average $Ni_3(NO_3)_2(OH)_4$ and NiO crystallite size was calculated according to the Scherrer equation from the 15° and 50.9° 2θ lines respectively.

Results and Discussion

Impregnation and drying of all samples resulted in the formation of a crystalline basic nickel nitrate phase ($Ni_3(NO_3)_2(OH)_4$). In Figure 1 the average crystallite sizes of the nickel phases, after drying and calcination, are depicted. For all samples the average $Ni_3(NO_3)_2(OH)_4$ crystallite size (Figure 1, ■) is close to the average pore diameter, indicating that this phase is confined by the pores. Upon decomposition of $Ni_3(NO_3)_2(OH)_4$ into NiO, the

average particle diameter is expected to shrink approximately 33%, due to the density difference and mass loss. However, air calcination (data not shown) resulted in average particle sizes ranging from 6-23 nm for the different samples, which exhibited broad particle size distributions and no simple correlation to the pore diameter. For the NO calcination, on the other hand, the NiO particle size scales with the pore size (Figure 1, ▼). NiO particle sizes smaller than the $Ni_3(NO_3)_2(OH)_4$ crystallite sizes were found, indicating fragmentation rather than agglomeration has occurred and the NiO was retained inside the mesopores. The applicability of tailoring metal oxide particle size to other supported metal catalysts such as cobalt and copper will be reported in the full paper.
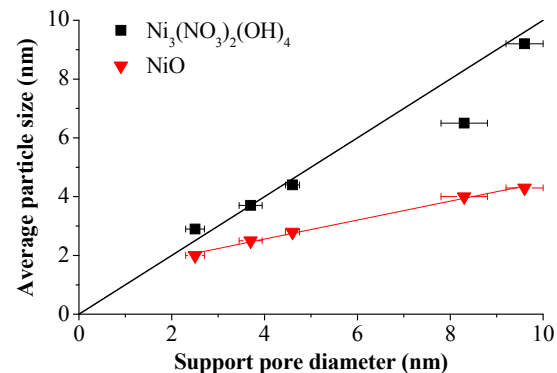
Figure 1. The relation between the support diameter and the $Ni_3(NO_3)_2(OH)_4$ crystallite size after drying at 120°C (■) and the NiO crystallite size after NO calcination (▼). The error bars indicate the full width half maximum of the pore size distribution.

Significance

Control over the preparation of catalysts is a key to optimize and to understand the catalytic activity of supported catalysts. Combining well defined mesoporous supports with NO-controlled decomposition of metal nitrates, control is obtained over the particle size at high metal loading.

References

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