New synthesis method for nickel phosphide hydrotreating catalysts

Shaofeng Yang and Roel Prins*

Received (in Cambridge, UK) 7th June 2005, Accepted 7th July 2005
First published as an Advance Article on the web 27th July 2005
DOI: 10.1039/b507940c

Nickel phosphide particles on silica and alumina support were prepared from metal or metal oxide particles by treatment with phosphine and hydrogen at moderate temperature, resulting in small particle sizes equivalent to that of the precursor particle size.

The need to deeply reduce the sulfur level of fuels has led to a high interest in materials different from the classic hydrotreating catalysts based on MoS_2. Metal carbides and nitrides are initially highly active, but are not stable in a sulfur-containing atmosphere.[1] Supported metal phosphides of W, Mo, Co and Ni can be prepared from the corresponding metal salts and $(NH_4)_2HPO_4$ by reduction in H_2 and the resulting materials have very promising hydrotreating activities.[2–8] Under hydrodesulfurization (HDS) conditions the surfaces of molybdenum and nickel phosphide take up sulfur atoms, but the kernels of the metal phosphide particles stay intact.[8–10] Unfortunately, the dispersion of thus-prepared supported metal phosphides is low, because the P–O bond is strong and its reduction requires high temperature. We have therefore looked for phosphor-containing species that contain P–X bonds that are easier to break than the P–O bond in phosphates and phosphites. We have found that supported metal phosphide particles of high dispersion can be obtained by treating reduced metal particles as well as metal oxide particles on a support by phosphine. In this method there is no need to go to high temperatures, and as a consequence the size of the metal phosphide particles is equivalent to that of the metal particles and can be kept small.

Silica-supported nickel phosphide was prepared by reaction of supported Ni and NiO particles with PH_3. The supported metal precursor was prepared by pore-volume impregnation. Aqueous solutions of nickel nitrate and nickel acetate were used in the impregnation. The corresponding samples are denoted as N–X (nitrate) and A–X (acetate) respectively, where X is the weight percent of nickel in the samples. The dried, impregnated N–X and A–X solids were reduced in flowing H_2 at 673 K for 2 h, followed by cooling down to 298 K in flowing H_2. The dried N–X precursors were also calcined at 773 K for 3 h before reduction in H_2. The reduced Ni/SiO_2 samples were exposed to a flowing 10% PH_3/H_2 mixture (20 ml min^{-1}) between 298 and 523 K; the final temperature was maintained for 2 h. Then the samples were cooled down to 298 K in flowing H_2, flushed with He for 20 min and passivated in a flow of 1 mol% O_2/He. In addition, a sample was prepared by the classical phosphate reduction method[2] for comparison (NP-13, nickel loading 13 wt%).

Fig. 1 shows the XRD patterns of the reduced N-13 Ni/SiO_2 precursor, prepared from nickel nitrate, after reaction with 10% PH_3/H_2 at different temperatures. After reaction at 298 K, the diffraction characteristics of Ni particles are still present, similar to those of the starting Ni/SiO_2 precursor. The Ni peaks almost disappeared after reaction at 323 K, only a broad Ni peak at *ca.* 44.6° remained. In the XRD pattern of the Ni/SiO_2 precursor after reaction with phosphine at 373 K intense peaks were present at 40.7°, 44.6° and 47.4° and weaker peaks at 54.2° and 55.0°, all attributed to Ni_2P.[4] Very weak peaks were present at 41.8°, 42.8°, 43.6° and 45.3°, corresponding to Ni_3P.[4] When the reaction temperature was increased to 423 and 523 K, only the Ni_2P diffraction peaks were present, indicating that pure Ni_2P can be prepared on silica by treatment with phosphine and hydrogen above 423 K.

Metallic Ni/SiO_2 precursors, prepared from different metal salts, were treated *in situ* with 10% PH_3/H_2 at 523 K. The crystallite sizes of the samples corresponding to the [111] diffraction at 40.7° were calculated using the Scherrer equation ($D = 0.9\lambda/\beta \cos\theta$). Fig. 2a shows that the XRD pattern of the catalyst prepared by the classical phosphate reduction method had sharp peaks; large Ni_2P particles with an average crystallite size of 30 nm had formed. The N-13 and N-5 Ni_2P/SiO_2 catalysts exhibited broader XRD peaks (Figs. 2b and c) with average crystallite sizes of 13 and 11 nm, respectively (the Ni particle sizes of their Ni/SiO_2 precursors were

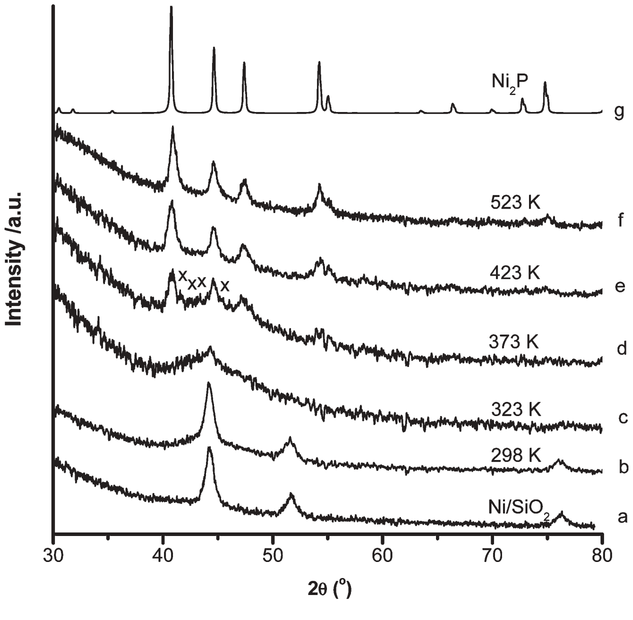

Fig. 1 XRD patterns of the 13 wt% Ni/SiO_2 precursor, prepared from nickel nitrate, after reaction with phosphine at different temperatures. x, Ni_3P.

Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology (ETH), 8093, Zürich, Switzerland.
E-mail: roel.prins@chem.ethz.ch; Fax: +41-44-6321162;
Tel: +41-44-6325490

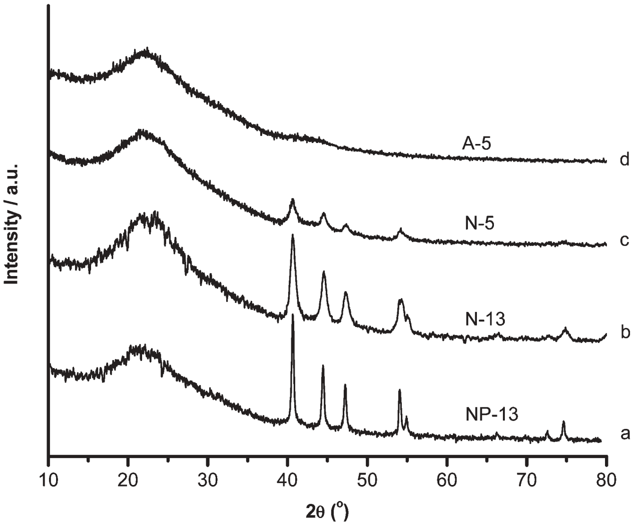

Fig. 2 XRD patterns of Ni_2P/SiO_2 catalysts prepared from different precursors.

10 and 8 nm). The XRD pattern of sample A-5 showed only the features of amorphous silica, implying that the nickel phosphide particles were too small to be detected by XRD. This could be further confirmed by the STEM image of Ni_2P/SiO_2 catalyst of sample A-5 (Fig. 3).

For the highly dispersed A-5 Ni_2P/SiO_2 catalyst, for which no XRD lines could be measured, NMR spectroscopy proved a powerful tool. The metallic character of metal phosphides leads to large ^{31}P NMR Knight shifts, which makes it easy to distinguish metal phosphides from diamagnetic phosphates.[4,6] ^{31}P MAS-NMR spectra were obtained with an Advance 400 WB Bruker spectrometer at room temperature. Samples were packed into a 4 mm diameter rotor in an inert atmosphere and measured with spinning at 12 kHz. The isotropic shifts of the signals were obtained by comparing spectra measured at different spinning rates. The Ni_2P structure contains two crystallographic P sites and consequently gives two resonances with isotropic chemical shifts of 1487 and 4076 ppm.[4] ^{31}P MAS-NMR spectra of the A-5 Ni_2P/SiO_2 catalysts prepared at 423 K showed peaks around 1478 and 4060 ppm, confirming that Ni_2P had formed.

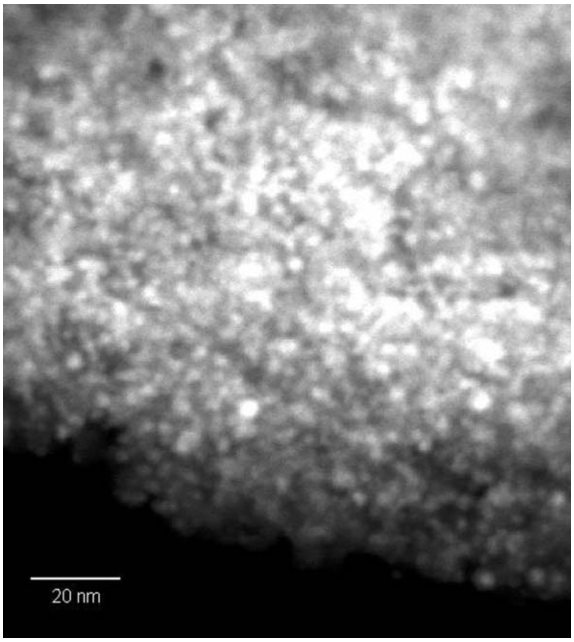

Fig. 3 STEM image of A-5 Ni_2P/SiO_2 catalyst.

To examine if PH_3 also reacted with supported NiO, the calcined 13 wt% NiO/SiO_2 sample was treated with a 10% PH_3/H_2 mixture at different temperatures. The XRD patterns show that, after reaction with phosphine at 523 K for 2 h, the NiO peaks had almost disappeared and that weak peaks at 40.7°, 44.6° and 47.4° attributed to Ni_2P were present. When the reaction temperature was increased to 623 K, only the diffraction peaks corresponding to Ni_2P were present. This indicates that silica-supported Ni_2P can also be achieved by treating a NiO/SiO_2 precursor with phosphine above 623 K.

In 1996 Robinson *et al.* described several methods to prepare Ni_2P and Co_2P and studied the HDN activity of quinoline of the resulting materials.[11] One of their preparation methods was the use of phosphine, but only a limited number of experiments was described. Our results demonstrate that metal phosphide particles on a support can very easily be prepared from metal or metal oxide particles by treatment with phosphine and hydrogen. In the case of Ni, the metal particles already became fully phosphided at 423 K, while NiO particles needed 623 K. These temperatures are very much lower than the temperatures required in the phosphate method of preparing metal phosphide. Because of the very strong P–O bond, temperatures of about 1000 K are needed.[2–6] Such high temperatures lead to the almost exclusive formation of phosphorus (phosphine is not stable at high temperature), which diffuses only slowly into the metal particles. All this leads to sintering and loss of dispersion.

At these high temperatures phosphate also reacts with supports like alumina and therefore a large excess of phosphate has to be added in order to make metal phosphide particles.[5,12] Thus, only alumina-supported nickel phosphide catalysts with low dispersions and loadings above 20 wt% have been reported.[12] The present phosphine method allows preparing highly dispersed metal phosphide particles even on an alumina support. This is an important result, because alumina is industrially preferred to silica since it is thermally much more stable. Fig. 4e shows the XRD pattern of the alumina-supported nickel phosphide catalyst (Ni loading 10 wt%) prepared by treating the metallic Ni/Al_2O_3 precursor (Fig. 4c) with a 10% PH_3/H_2 mixture at 523 K. *In situ* NMR measurements on the γ-Al_2O_3 support after treatment with PH_3 at 573 K for 2 h showed no phosphate peaks around 0 ppm. This indicates that the alumina support was not phosphided.

The hydrotreating activities of the A-5 and N-13 Ni_2P/SiO_2 catalysts were tested in the HDN of *o*-methylaniline (OMA) and HDS of dibenzothiophene (DBT) at 613 K and 3.0 MPa. The passivated catalysts (0.2 g, diluted with 8 g SiC) were activated *in situ* with H_2 at 673 K and 0.1 MPa for 3 h. Reactions were carried out in a continuous–flow microreactor as described before.[6,13] The composition of the gas-phase feed consisted of 130 kPa octane or toluene (used as the solvents for HDN and HDS, respectively), 17 kPa heptane (as reference for OMA and its derivatives in the GC analysis) or 8 kPa dodecane (as reference for DBT and its derivatives in the GC analysis), and about 2.8 MPa H_2. For each of the catalysts, the HDS reaction was carried out

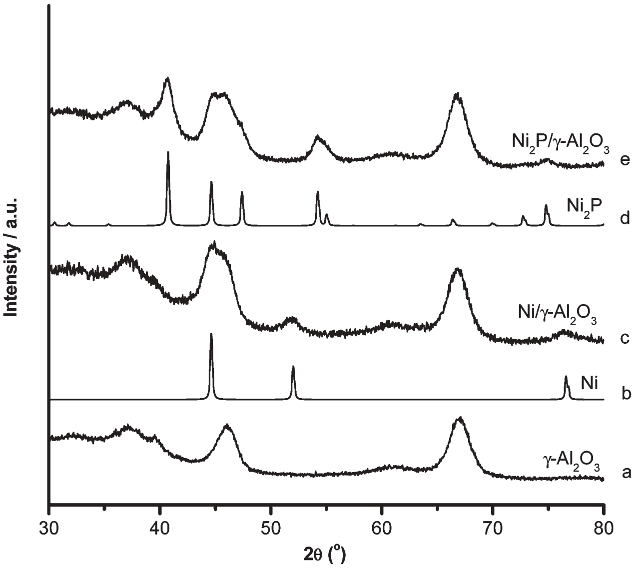

Fig. 4 XRD patterns of alumina support (a), Ni/Al$_2$O$_3$ precursor (c), Ni$_2$P/Al$_2$O$_3$ catalysts prepared by treating (c) with phosphine at 523 K (e), and calculated patterns of Ni (b) and Ni$_2$P (d).

subsequent to the HDN reaction, without changing the catalyst. The reaction products were analyzed by off-line gas chromatography. The catalyst was stabilized at 613 K and 3.0 MPa for at least 48 h before samples were taken for analysis.

The hydrotreating reaction results for the A-5 and N-13 Ni$_2$P/SiO$_2$ catalysts are summarized in Table 1. The data were taken at the weight time[13] of 40 g min mol^{-1} for OMA HDN and 20 g min mol^{-1} for DBT HDS. The HDN activities of both Ni$_2$P catalysts were very good and much higher than that of the metal phosphide catalysts determined before.[6] Also the activities of both Ni$_2$P catalysts in the HDS of DBT were very high. They are higher than that of the Ni$_2$P/SiO$_2$ catalyst described by Wang *et al.*[14] Wang *et al.* observed a conversion that was 1.4 times higher than ours. Assuming a first order rate equation, taking into account that they used 11.7 times more catalyst, and that the HDS of DBT was carried out at 613 K in our study and at 643 K in their study, we estimate that our catalyst is about one order of magnitude more active than that of Wang *et al.*

The product distribution (the selectivity of biphenyl is very high) shows that DBT is mainly desulfurized by the DDS route over phosphide catalysts. This is similar to that over sulfided CoMo and NiMo catalysts. But it should be noted that the selectivity of biphenyl over the A-5 Ni$_2$P/SiO$_2$ catalyst (95% at the lowest and 92% at the highest weight time) is much higher than that over sulfided catalysts, which is 70 ~ 80% in general.[13] This could be due to the small particle size of the A-5 Ni$_2$P/SiO$_2$ catalyst, which enhances the σ adsorption of DBT molecules on the active sites. The amount of tetrahydro-DBT was very low, showing that it is easily desulfurized. The further hydrogenation of cyclohexylbenzene to bicyclohexyl did not take place.

Table 1 Hydrotreating performance of Ni$_2$P/SiO$_2$ catalysts

	Conversion (%)			Selectivity (%)	
Reaction	A-5	N-13	Product	A-5	N-13
HDS of DBT	65	82	Biphenyl	93	85
			Cyclohexylbenzene	6	14
			TH-DBT	1	1
HDN of OMA	76	90	Methylcyclohexane	75	59
			Methylcyclohexene	10	5
			Toluene	12	34
			Ethylcyclopentane	3	2

The phosphine method allows preparing metal phosphide particles at moderate temperature. As a result, the particle size is equivalent to that of the precursor particle size and small supported metal phosphide particles can be made of any metal or metal oxide precursor that can be made with high dispersion. Even on alumina, low-loading metal phosphide catalysts with high dispersion and high activity can be made.

The authors thank Dr. Changhai Liang for performing the hydrotreating measurements.

Notes and references

1 R. Prins, *Adv. Catal.*, 2001, **46**, 399.
2 P. Clark, W. Li and S. T. Oyama, *J. Catal.*, 2001, **200**, 140.
3 D. C. Phillips, S. J. Sawhill, R. Self and M. E. Bussell, *J. Catal.*, 2002, **207**, 266.
4 C. Stinner, Z. Tang, M. Haouas, Th. Weber and R. Prins, *J. Catal.*, 2002, **208**, 456.
5 P. A. Clark and S. T. Oyama, *J. Catal.*, 2003, **218**, 78.
6 V. Zuzaniuk and R. Prins, *J. Catal.*, 2003, **219**, 85.
7 S. T. Oyama, *J. Catal.*, 2003, **216**, 343.
8 Y. Shu and S. T. Oyama, *Chem. Commun.*, 2005, 1143.
9 Z. Wu, F. Sun, W. Wu, Z. Feng, C. Liang, Z. Wei and C. Li, *J. Catal.*, 2004, **222**, 41.
10 K. A. Layman and M. E. Bussell, *J. Phys. Chem. B*, 2004, **108**, 10930.
11 W. R. A. M. Robinson, J. N. M. van Gestel, T. I. Koranyi, S. Eijsbouts, A. M. van der Kraan, J. A. R. van Veen and V. H. J. de Beer, *J. Catal.*, 1996, **161**, 539.
12 S. J. Sawhill, K. A. Layman, D. R. Van Wky, M. H. Engelhard, C. Wang and M. E. Bussell, *J. Catal.*, 2005, **231**, 300.
13 M. Egorova and R. Prins, *J. Catal.*, 2004, **225**, 417.
14 X. Wang, P. Clark and S. T. Oyama, *J. Catal.*, 2002, **208**, 321.