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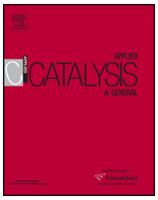

Improving the sintering resistance of Ni/Al_2O_3 steam-reforming catalysts by promotion with noble metals

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ABSTRACT

The role of Rh, Ir and Ru promoters on the structural properties and catalytic behavior of $Ni/\alpha\text{-}Al_2O_3$ catalyst during steam methane reforming (SMR) was investigated. The catalysts were subjected to aging treatments at 800 °C and $P_{H_2O} = 22$ bar *g* in order to induce sintering of the metal nanoparticles and alloying between Ni and the promoters. The crystallite sizes and the extent of alloying were determined in the reduced and aged catalysts by combination of in situ extended X-ray absorption fine structure (EXAFS), X-ray powder diffraction (XRPD), transmission electron microscopy (TEM) and X-ray energy dispersive spectroscopy (STEM-XEDS) mapping. The results reveal that the degree of alloying between Ni and Rh or Ir promoters increases during the aging process, as a result of the high mobility of the nickel species and diffusion into the FCC structures of Rh and Ir. Moreover, the formation of Ni–Rh and Ni–Ir alloy particles has a positive effect in mitigating the sintering of the nickel particles. In contrast, sintering inhibition effect of Ru was poorer due to its lower miscibility in nickel as well as its lower sintering resistance under the aging conditions employed. Based on density functional theory (DFT) calculations the diffusion of the Ni atoms into the lattice structure of Ru is energetically not favorable, whereas Ni atoms are equally stable in the first and second surface layers of Ir and Rh. Hence, a synergistic effect between Ni and Rh or Ir is achieved due to the alloy formation leading to conservation of larger active metal surface area and consequently to superior SMR activity with respect to the monometallic systems.

1. Introduction

Supported nickel catalysts are widely used in the steam reforming process for industrial scale production of synthesis gas (i.e., CO, H_2 and CO_2), which is subsequently converted into, e.g., methanol, ammonia, hydrogen or transportable fuels [1]. Due to the harsh reaction conditions under steam reforming operation (high *T* and high steam *P*) the active nickel nanoparticles are subjected to gradual sintering, thereby losing effective surface area and catalytic activity [1,2]. The sintering of the nickel particles as a function of time, temperature, steam and H_2 pressures and type of support have been previously investigated in detailed by Sehested et al. [3,4], revealing that above ca. 700 °C sintering via Ostwald ripening dominates the sintering rate of Ni/Al_2O_3 catalysts at high *P* (40 bar) under $H_2O:H_2$ atmospheres.

The use of different noble metal promoters (Pt, Pd, Rh, Ru, Ir, etc.) in nickel-based catalysts for the methane steam reforming (SMR) and autothermal reforming (ATR) processes have been previously addressed in the literature by several groups, who have reported different promotional effects such as an increase in the NiO reducibility, enhanced nickel dispersion, improved resistance to re-oxidation under oxidative steam reforming conditions, and superior coke resistance [5–20]. In some cases the studies suggested various degrees of interaction between the nickel and the noble metals although the influence of the noble metal on the physicochemical and catalytic properties of the Ni particles and the exact interplay between the metals remained unclear.

The present works intends to present a systematic study to address the interaction between various noble metals and the nickel particles in terms of degree of alloying and the effect on the catalytic properties. The aim of this study was namely, to investigate the differences among Rh, Ir and Ru when used as promoters for $Ni/\alpha\text{-}Al_2O_3$ catalyst systems and their influence on the nickel metal particle size and the sintering resistance. The catalysts have been studied both in the reduced and aged states by combination of various bulk characterization techniques, as well as by density functional theory (DFT). The aging treatments were performed to simulate long-term exposure to industrial conditions, thereby inducing sintering and alloying of the metal nanoparticles.

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2. Experimental

2.1. Catalyst preparation and post-treatments

The starting support material is α-Al_2O_3 with low porosity (<25%), small pore volume (<100 ml/kg) and low surface area (<1.5 m^2/g). The support was sieved to particles with fractions in between 0.42 and 0.50 mm and loaded with 3.0 wt% Ni in a single step of incipient wetness impregnation (IWI) using an aqueous solution of $Ni(NO_3)_2 \cdot xH_2O$, followed by calcination in air at 450 °C for 1 h. Loading of the noble metals was done by IWI using aqueous solutions of $Rh(NO_3)_2 \cdot xH_2O$, $IrCl_3 \cdot 6H_2O$ and $Ru(NO_3)_3(NO)$ to obtain approximately 0.5–1.0 wt% noble metal. The α-Al_2O_3 support was also impregnated directly with the noble metals in order to prepare monometallic catalysts as references. The catalysts were finally calcined in air at 450 °C for 1 h and reduced in H_2 flow at 525 °C for 2 h, with the exception of the Ru/Al_2O_3 and Ni–Ru/Al_2O_3 catalysts, for which the calcination step was omitted and the reduction was carried out directly after impregnation and drying at 80 °C. After reduction, a final passivation was conducted by means of feeding small pulses of O_2 in N_2 flow at RT. An overview of all the catalyst systems prepared is given in Table 1.

The aging treatments were carried out under conditions of 800 °C, 30 bar g and steam/H_2 atmospheres (H_2O/H_2 ratio = 6) during a period of 240 h.

2.2. Catalyst testing

The catalytic properties of the reduced/passivated and aged catalysts were tested in the methane steam reforming (SMR) reaction at low T (500 °C) in order to avoid mass-transfer limitations and to provide values of the relative intrinsic activities. The tests were performed in an 8.5 mm diameter quartz reactor tube containing the catalyst sieved into fractions between 0.125 and 0.300 mm and mixed with inert material. The reactor was initially heated from RT to 500 °C at a rate of 5 °C/min under pure H_2 flow at 2 bar g, and at 500 °C the gas composition was adjusted to 8 Nl/h H_2O, 2 Nl/h CH_4 and 0.8 Nl/h H_2 resulting in a gas hourly space velocity (GHSV) of 11,195 h^{-1}. These inlet conditions were maintained during the rest of the activity test. After the catalytic tests at 500 °C for 1 h, the reactor was heated to 800 °C at a rate of 5 °C/min and held 1 h. The reactor was finally cooled to 500 °C for measuring the final SMR activity. This protocol was followed to avoid SMSI effects occurring between the pure noble metal particles and the support, which could partially poison the surface and decrease the catalytic activity [21]. The product composition at the reactor outlet was analyzed on-line by gas chromatography throughout the measurements.

2.3. Catalyst characterization

X-ray powder diffraction (XRPD) was measured ex situ using Cu Kα radiation and Bragg–Brentano geometry (PANalytical XpertPro). The data was used to determine the metal crystallite sizes and the extent of alloying by measuring the lattice constants of the different metallic particles. Rietveld refinements were performed for the quantitative analyses.

The extended X-ray absorption fine structure (EXAFS) spectra at the Ir L_3-edge (1,215 eV), Rh K-edge (23,220 eV) and Ru K-edge (22,117 eV) were collected in Hasylab (Hamburg) during in situ reduction treatments of both the reduced and the aged catalysts in order to ensure a fully reduced state at the surface of the metal particles. The reactor was loaded with the required amount of catalyst powder, which was sieved as 75–125 μm fractions to enable plug-flow gas conditions. The in situ reduction treatment was conducted in 20% H_2/He atmospheres from RT to 550 °C at a rate of 5 °C/min. After 2 h reduction at 550 °C, the reactor was cooled to RT and the EXAFS scans were collected under the same gas composition. The scans were performed in transmission geometry, using the double Si(3 1 1) or Si(1 1 1) crystal monochromators and a beam size of 1 × 8 mm^2. Rh, Ir and Ni foils were used as internal standards for energy calibration. The EXAFS refinements were performed with the EXCURV software [22] using k^3 weighting in the range 2.5–12.5 $Å^{-1}$ for the three absorption edges. Phase shifts and backscattering factors were calculated ab initio using Hedin–Lundqvist potentials. AFAC parameters (amplitude reduction factor) were determined from the Rh (0.83), Ir (0.84) and Ru (0.867) foils.

Transmission electron microscopy (TEM) images in bright-field mode and STEM-XEDS (X-ray energy dispersive spectroscopy) chemical maps were acquired on the fresh and aged catalysts using a CM-200 TEM-microscope coupled with a Si–Li EDS detector and a Fischione high angle annular dark field detector. At least four maps from random areas were taken for each catalyst. The STEM probe size was 1.7 nm and the pixel size in the maps was set to 2 nm with an acquisition time of 1–1.3 s per pixel. The samples were prepared by finely crushing the catalyst pellets and then immersing a Cu grid containing a holey-carbon film into the powder.

Density functional theory (DFT) was used to obtain segregation energies of Ni in Rh, Ru and Ir. The energies were obtained using the DACAPO-code, where exchange-correlation effects were described by employing the RPBE generalized gradient correction self-consistently [23]. The Kohn–Sham one-electron valence states were expanded in a basis of plane waves with kinetic energies up to 340 eV (30 Ry) and a density cutoff of 540 eV. Vanderbilt non-local ultrasoft pseudopotentials were used to treat the ionic cores [24]. A 4 × 4 × 1 Monkhorst–Pack k-point sampling in the irreducible Brillouin zone was used [25]. The slab was modeled with a 2 × 2 unit cell with four layers, where the two top layers were allowed to relax. The segregation of Ni from the second to the first surface layer of the (1 1 1) metal facets of Ru, Rh and Ir was calculated. The segregation energy was obtained from: $\Delta E = E_A - E_B$, where E_A is the energy of the metal slab (Rh, Ru or Ir), with Ni in the first surface layer, and E_B the energy of the metal slab with Ni in the second layer. Also the effect on the energy for varying fractions of Ni in the surface layers was calculated. The segregation energy of Rh, Ru and Ir from the second to the first surface layer of the Ni(1 1 1) metal surface was also calculated in the same manner.

Table 1
Overview of Ni/Al_2O_3 catalyst under study along with the noble metal loadings as measured by ICP. All the catalysts contain 2.9 wt% Ni.

Catalyst code	Loading (wt%)			
	Ni	Ir	Rh	Ru
Ni/Al_2O_3	2.89	–	–	–
Ir/Al_2O_3	–	0.94	–	–
Ni–Ir/Al_2O_3	2.91	0.97	–	–
Rh/Al_2O_3	–	–	0.98	–
Ni–Rh/Al_2O_3	2.92	–	1.12	–
Ru/Al_2O_3	–	–	–	0.52
Ni–Ru/Al_2O_3	2.92	–	–	0.53

3. Results

3.1. TEM

Representative low-magnification bright-field images collected for the fresh aged catalysts are displayed in Figs. 1 and 2, respectively. The images reveal large differences in particle size distributions in the four systems. In the fresh Ni/Al_2O_3 only medium–large particles are seen typically larger than 20 nm,