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Activation mechanism and microstructural evolution of a YSZ/Ni-alumina catalyst for dry reforming of methane

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ABSTRACT

Ni-doped alumina spinels are known catalysts for hydrocarbons reforming that are typically synthetized by reacting Ni nitrates with γ–Al_2O_3. It is believed that Ni particles (the active phase) are reduced from $NiAl_2O_4$ once subjected to reaction. Here, we revisit the mechanisms of Ni particles formation from Ni-alumina catalysts by X-ray diffraction (XRD) and transmission electron microscopy (TEM) of fresh and used catalysts. We also monitored the evolution of the catalyst's crystalline structure exposed to reactants, by *in situ* XRD. Ni-alumina catalyst structure can be explained by a tetragonal ($I4_1/amd$ space group) spinel phase with Al (or Ni cations) occupying $4a$, $8c$ and $8d$ Wyckoff sites. Ni is initially distributed homogeneously in the alumina platelets. The alumina from the fresh catalyst is initially cubic, but under reducing conditions typical to reforming (CO_2:CH_4 = 1:1 at 850 °C), the c/a ratio decreases and the sites occupancy changes. After 12-days reaction, facetted nanoparticles are formed and share an interface with tetragonal alumina platelets with the following crystalline relationships: $Ni_{(110)} \| Ni_xAl_yO_{4(20\bar{2})}$ and $Ni_{(111)} \| Ni_xAl_yO_{4(20\bar{2})}$. This study brings valuable insight into the activation mechanism and microstructural evolution of a yttria-stabilized-zirconia/Ni-alumina catalyst to understand the behaviour of other spinel catalysts.

1. Introduction

Metal aluminate spinels are known catalysts for various hydrocarbon reforming processes [1–3] produced according to various methods, such as co-precipitation [4,5], sol-gel [6] and wet impregnation [7]. In almost every case, synthesis is followed by a calcination step to produce spinels. Ni clusters, the active phase, are believed to be expressed at the surface of supports in conditions typical of hydrocarbon reforming operations [8,9] or after an activation step at high temperature under H_2 [10,11]. It is known that various steps involved in the preparation of Ni/alumina catalysts will control the metal's size, distribution and reducibility. In turn, these physico-chemical properties participate in metal-support interactions which are key to controlling catalytic activity [12].

Our group previously developed and investigated Ni-supported catalysts [8,9,13]. These papers highlighted the relationship between the preparation methods and the formulations with catalyst properties and performance. Catalytic activity was studied under different reforming conditions, showing high activity and stability for extended periods. The effect of yttria-stabilized-zirconia (YSZ) as a co-support in Ni spinel aluminate formulation was also investigated [13]. Interestingly, when a mixture of alumina and YSZ was impregnated with Ni nitrates, Ni preferentially deposited on YSZ particles because of favorable interaction. YSZ had two fundamental outcomes: (i) it prevented premature deactivation and (ii) its presence favored formation of the Ni-alumina spinel phase during the calcination step. In fact, without YSZ, other alumina polymorphs, such as $NiAl_{10}O_{16}$, were formed upon calcination.

The type and relative amount of alumina are known to impact spinel formation after calcination. According to several reports [14,15], the spinel structure γ–$Al_{2.67}O_4$ facilitates the formation of metal spinel with respect to other alumina polymorphs. With Ni:Al atomic ratio in excess of 1:2, NiO forms and quickly leads to coking and deactivation. Active hydrocarbon reforming phases are rather obtained with substoichiometric ratios of NiO to Al_2O_3 [10]. In this case, a solid-state reaction between NiO and Al_2O_3 occurs during calcination and results in Ni-doped alumina or metal-deficient spinel. Moving towards the alumina side of the NiO–Al_2O_3 tie-line leads to symmetry breaking of the cubic structure [16]. A similar behavior has been observed with other metal-alumina systems,

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such as $MgO–Al_2O_3$. In this case, tetragonal (space group $I4_1/amd$) and orthorhombic (space group $P222$) phases were detected below 5.5 at.% and 0.1 at.% MgO, respectively [16].

Although a strong body of evidence demonstrates formation of the metal-deficient spinel phase upon calcination, not much attention has been paid to the activation step. The mechanisms involved during calcination are similar to those occurring during the activation phase, except that, under reducing conditions, metallic Ni becomes an active component of the system. Upon formation of the Ni, alumina is also expected to evolve and will eventually impact the catalytic activity. For instance, Ni particles from spinel reduction are known to be highly dispersed and delay sintering. Given the dependence of Ni sintering on the nature and morphology of supports [17], it is critical to understand and ascertain the nature of the resulting alumina and characterize the interface it shares with Ni.

This report probes the structure of alumina and various other phases during the activation step. Using *in situ* X-ray diffraction (XRD) and transmission electron microscopy (TEM), we propose a model that describes the interplay between Ni-deficient spinel aluminate and alumina during the activation step. In this study, the nature of the interfacial relationship between metallic Ni and Ni-depleting matrix is also investigated.

2. Experimental

2.1. Catalyst preparation and reforming reaction

The catalyst was prepared according to the wet-incipient method. YSZ (containing 7% of yttria) and γ-Al_2O_3 in powder form were mixed with Ni nitrates (47.5 wt.% YSZ, 47.5 wt.% Al_2O_3 and 5 wt.% Ni) and calcined at 900 °C for 1 h, employing a procedure developed previously by our group [8,18]. 0.897 g of catalyst was initially exposed to mildly-reducing reforming conditions for 1 h ($CO_2:CH_4:H_2O = 0.8:1:0.1$, with a feed rate of 94 mL/min) at 850 °C and then for 12 days in a typical reforming condition ($CO_2:CH_4:H_2O = 1:1:0.1$) (mean gas hourly space velocity (GHSV) of 26,000 $mL/h/g_{cata}$ under reaction conditions). CO_2 and CH_4 conversions were monitored by gas chromatography.

2.2. Temperature-programmed reduction (TPR) of fresh catalyst

The fraction of Ni-reducible species was determined by TPR of the fresh catalyst. Analysis was undertaken using a ChemiSorb 2750 from Micromeritics. The apparatus was calibrated with Ag_2O for H_2 consumption quantification, under the same analytical conditions. 0.1004 g of sample was heated to 300 °C (10 °C/min) under pure helium flow (40 sccm) and held for 3 h to remove physisorbed species, then cooled to room temperature. TPR was performed immediately after this pre-treatment under 10% H_2 in Ar (40 sccm), with a ramp of 10 °C/min from room temperature to 1100 °C.

2.3. TEM of fresh and used catalyst

A drop of ethanol suspension of fresh and used samples was left to dry on a 200-mesh holey carbon copper grid. TEM was undertaken in high angle annular dark field scanning (HAADF-STEM) mode, using a FEI F20 high-resolution TEM system. Electron energy loss spectroscopy (EELS) in STEM mode and associated HAADF micrography of used catalyst was done using an FEI Titan TEM operated at 300 kV and equipped with Gatan Image Filter Quantum. Elemental maps of O and Ni were produced by integrating background-subtracted O K and Ni $L_{2,3}$ edges of EELS collected for each pixel over the region of interest.

Table 1
Alumina and nickel alumina phases considered for Rietveld refinement.

Formula	Space group (number)	PDF no	Common name
Al_2O_3	$P4_12_12$ (92)	04–008-4096	δ alumina
Al_2O_3	$C2/m$ (12)	04–008-7261	θ alumina
Al_2O_3	$P222$ (16)	00–046-1215	δ^0 alumina
Al_2O_3	$R\bar{3}c$ (167)	04–005-4505	α corundum
Al_2O_3	$Pna2_1$ (33)	04–012-6907	κ alumina
Al_2O_3	$P\bar{4}m2$ (115)	04–016-7505	δ^* alumina
Al_2O_3	$Fm\bar{3}m$ (225)	04–016-1445	γ' alumina
$Al_{2.67}O_4$	$Fd\bar{3}m$ (227)	04–007-2615	η alumina
$Al_{2.67}O_4$	$I4_1/amd$ (141)	04–015-7830	γ alumina
$Al_{2.67}O_4$	$P6_3/mmc$ (194)	04–016-0539	
$NiAl_2O_4$	$Fd\bar{3}m$ (227)	04–007-5978	

2.4. In situ XRD–from fresh to used catalyst

A sample of fresh catalyst was analyzed with a PANalytical X-ray diffractometer operated in the Bragg-Brentano configuration with Cu K_α radiation (1.54056Å). Reforming reaction conditions were reproduced in a XRD reaction chamber (Anton Paar XRK 900). About 0.14 g of sample was first heated to 850°C under Ar for about 1 h. The catalyst was then exposed for 55 min to a reducing gas mixture of $CO_2:CH_4 = 0.8:1$ with a feeding rate of 15 sccm. A mixture of $CO_2:CH_4 = 1:1$ was then fed at a rate of 15 sccm to the reactor for 4.1 h, to represent reforming conditions as closely as possible. XRD patterns were collected in the range $2\theta = 25 - 82$ with step size of 0.04 and 49.725 s/step with a PIXcel 1D detector. After 1 h, changes in features became minor, and the scans were averaged 5 at a time to enhance the signal-to-noise ratio. The last 5 scans were taken over a period of 26.3 min, following time-on-stream of ~221 min (4.1 h) and are referred to as "cat4h".

Rietveld refinement was achieved with cubic ZrO_2 (PDF 04-002-8314), tetragonal ZrO_2 (PDF 04-005-4207) and monoclinic ZrO_2 (PDF 04-004-4339), Ni (PDF 04-10-6148) and NiO (PDF 04-014-0442) phases. Alumina and Ni-alumina phases were matched against the phases listed in Table 1. As expected from previous work [13], no evidence of interactions between Ni and YSZ constituents was found. Lattice parameters were refined to allow lattice expansion at 850°C. Rietveld refinement was carried out with PANAnalytical HighScorePlus software (v3.0.5). Quality of fit was evaluated by visual inspection of difference plots, agreement indices (Goodness-of-fit, expected R, R profile) and estimated standard deviation of individual parameters.

3. Results

3.1. Fresh catalyst analysis

HAADF-STEM micrography of a sample of the fresh catalyst (Fig. 1) shows micron-size platelets of porous alumina with homogeneous contrast. Recalling that contrast in HAADF-STEM scales roughly with the square of atomic number, Ni segregation in alumina should otherwise be obvious on the nanometer scale according to this technique (see insert in Fig. 1). Microscopy suggests that Ni is integrated at the atomic level of the alumina and forms a single phase. This is consistent with previous X-ray photoelectron spectroscopy (XPS) analyses of fresh catalyst produced with the same protocol [8].

The fractions of Ni reducible species of fresh catalyst was characterized by TPR (Fig. S1). A single peak above 800°C dominates the profile and is ascribed to γ–NiO, which is Ni interacting strongly with alumina [12,19,20]. For this sample, the fraction of reducible Ni is 4.34 wt.% when considering the reaction of 1 mol of H_2 reducing 1 mol of NiO. This value is in reasonable agreement with the amount of Ni introduced in the sample (5 wt.%).

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