

Influence of rare earth (RE=La, Pr, Nd, Gd and Sm) metals on the methane decomposition activity of Ni-Al catalysts

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(A). Preparation of catalysts:

The Ni:RE:Al with a layered HT-like anionic clay structure was obtained by the co-precipitation method. Two solutions namely (A) containing the required amount of metal (Ni, RE and Al nitrates corresponding to give (Ni:RE:Al=2:0.1:0.9 molar ratio) and solution (B) containing the precipitating agents (i.e. 1:1 of 2M NaOH and 1M Na₂CO₃) were added slowly and simultaneously into a beaker containing distilled water, while maintaining a constant pH~9 under vigorous stirring at room temperature. Thus, produced precipitate was thoroughly washed with distilled water until the pH reached to the pH of distilled water. The gel is filtered, dried at 100°C for 12 h and subsequently calcined in static air at 550°C for 5h.

(B). Characterization of catalysts:

The XRD patterns of the samples were obtained on a Rigaku miniflex X-ray diffractometer using Ni filtered Cu K α radiation ($\lambda=1.5406\text{\AA}$) from $2\theta=10$ to 80° at a scan rate of $2^\circ/\text{min}$ with the beam voltage and a beam current of 30kV and 15mA respectively. The surface areas of the fresh catalysts were measured by N₂ physical adsorption at -196°C in an Autosorb-I (Quantachrome) instrument. The specific surface area was calculated applying the BET method. The SEM images of the fresh and used catalysts were recorded using a JEOL-JSM 5600 instrument. For TEM analysis the samples dispersed in methanol solution and suspended on a 400-mesh, 3.5mm diameter Cu grid and images were taken using JEOL JEM 2010 high-resolution transmission electron microscope. The Raman spectra for the structural characterization of deposited carbon in deactivated catalysts have been acquired with a Horiba Jobin-Yvon lab ram HR spectrometer using a laser beam excitation of $\lambda=632.81\text{nm}$. Prior to O₂ pulse chemisorption measurements the sample reduced at 550°C in H₂ stream for 2h then it was cooled to 260°C in helium gas, outgassed at this temperature for 30 min, followed by titration with 5.01% O₂ in helium gas at 260°C . The O₂ uptakes on reduced Ni:RE:Al samples were calculated assuming the formation of NiO phase [25]. The infrared spectra were recorded between 4000 and 400 cm^{-1} at room temperature in a Agilent Cary600 FT-IR spectrometer. The carbon analyses of deactivated catalysts are collected with VARIO EL analyser instrument. The UV-Vis spectra were recorded at room temperature using a UV-2000, Shimadzu Spectrophotometer equipped with a diffuse reflectance attachment with an integrating sphere containing BaSO₄ as a reference. The spectra were recorded in the range between 190 and 800 nm with sampling interval 0.5 nm and slit width 2 nm and spectra were converted to Kubelka-Munk function. The ESR analysis of reduced Ni:RE:Al (2:0.1:0.9) samples were performed at room temperature using JEOL/JES-FA200 spectrophotometer by X-band equipment with an operating frequency $\nu = 9.029\text{ GHz}$. The TPR analysis was carried out in a quartz micro-reactor interfaced to GC with TCD unit. About 50mg was loaded in an isothermal zone of a quartz reactor (i.d = 6mm, length = 30 cm) heated by an electric furnace at a rate of $10^\circ\text{C}/\text{min}$ to 300°C in flowing helium gas at a rate of 30 cc/min. After degassing the sample was cooled to room temperature then the helium gas switched to 5% H₂ in argon (30 cc/min) and the temperature was increased to 700°C at a ramping rate of $5^\circ\text{C}/\text{min}$. Hydrogen consumption measured by analyzing effluent gas by means of thermal conductivity detector, and the H₂ uptakes were estimated with TPR of Ag₂O under similar protocol. The elemental analysis of calcined Ni-RE-Al samples were analysed by atomic absorption spectroscopy (AAS) Perkin Elmer, Analyst-300. The XPS measurements were carried out using a Thermo Scientific K-Alpha X-ray Photoelectron Spectrophotometer. All binding energies of interest were referenced to the carbon C 1s peak at 284.6 eV.

(C). Catalytic tests:

The CDM activities were performed in the temperature range of 500 to 650°C at atmospheric pressure in a fixed-bed vertical quartz reactor (i.d= 2cm, length = 46cm), operated in a down

flow mode. Methane supplied by Bhuruka gases limited (99.99%) is used directly without any diluents gas such as He. The experimental conditions used were as reported earlier with catalyst a charge of 30mg, CH₄ flow rate = 30 mL/min, *i.e.* GHSV of 180 L/h g_{cat}. Prior to the reaction, the catalyst was reduced at temperature range of 550°C with 5% H₂ in N₂ for 2 h. The reaction was continued until all the catalysts were completely deactivated. The catalysts were weighed before and after each experiment. The outflow gas was analyzed by Varian CP-3800 GC with TCD. The mass balance was done by CH₄ conversion, H₂ yields and the carbon accumulation on deactivated catalysts

(D). Thermodynamic equilibrium curve:

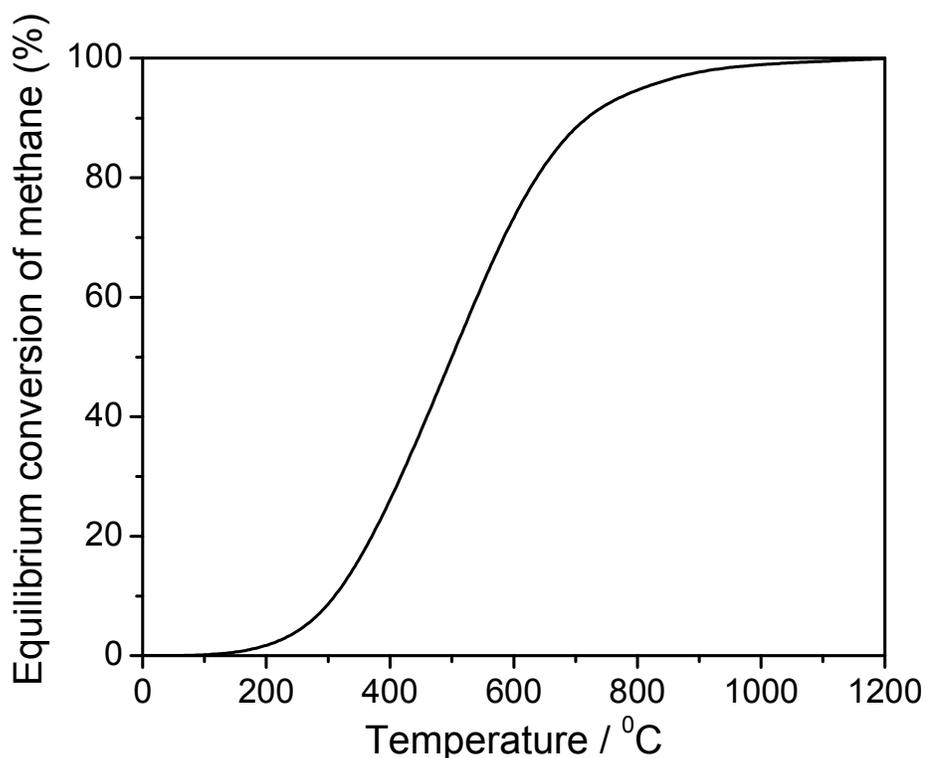


Figure 1: The equilibrium conversion of methane as a function of the reaction temperature for methane decomposition. Initial composition of the reaction mixture and the pressure are 100% CH₄ and 1 bar, respectively.

(E) TGA and DTA of oven dried samples

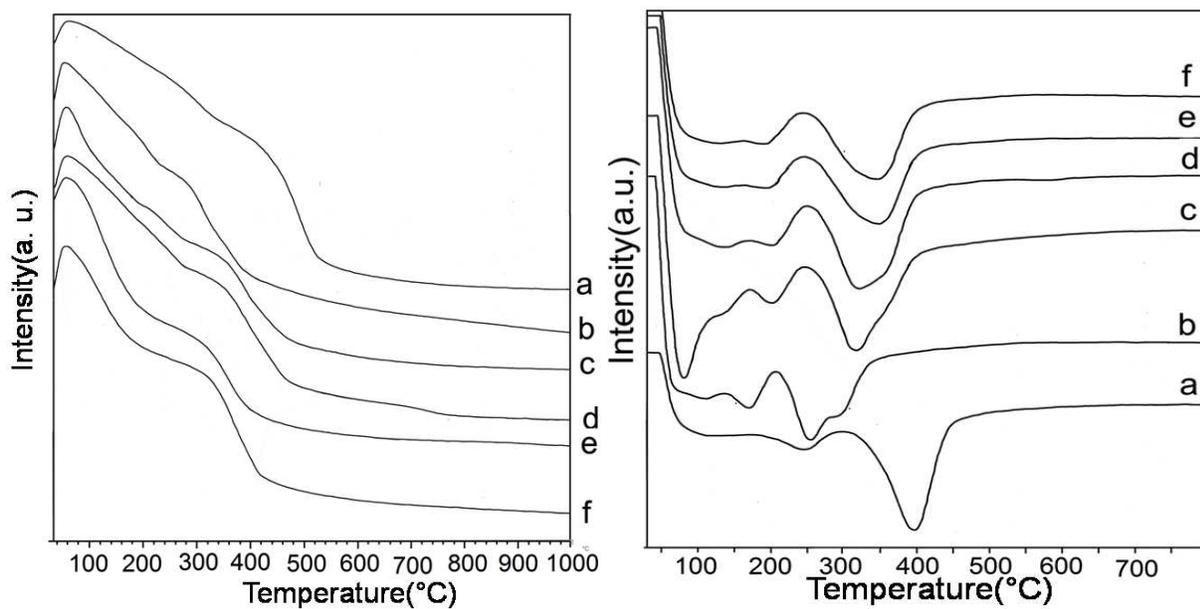


Figure 1: TGA-DTA profile of oven dried (a) Ni:Al (2:1), (b) Ni:La:Al (2:0.1:0.9), (c) Ni:Pr:Al (2:0.1:0.9), (d) Ni:Nd:Al (2:0.1:0.9), (e) Ni:Sm:Al (2:0.1:0.9) and (f) Ni:Gd:Al (2:0.1:0.9 mole ratio) samples

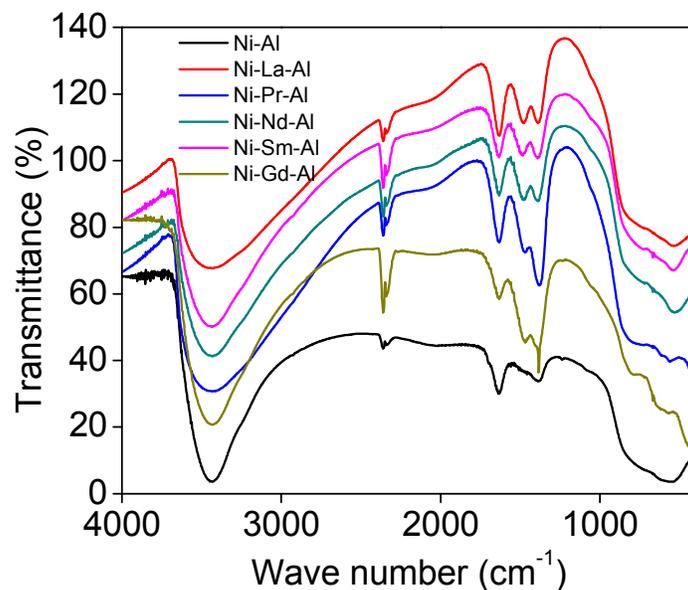
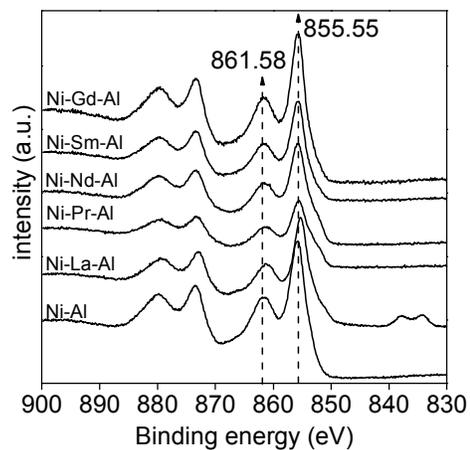


Figure 2: FT-IR spectra of reduced (a) Ni:Al (2:1), (b) Ni:La:Al (2:0.1:0.9), (c) Ni:Pr:Al (2:0.1:0.9), (d) Ni:Nd:Al (2:0.1:0.9), (e) Ni:Sm:Al (2:0.1:0.9) and (f) Ni:Gd:Al (2:0.1:0.9) samples

The FT-IR spectra of reduced samples are shown in Figure 2. The broad band observed at 3450 -3660 cm^{-1} is ascribed to the presence of hydrogen bonded OH. The band centered around 448 cm^{-1} is the Ni-O stretching mode.

Figure 3: The Ni 2p XP spectra of reduced Ni-RE-Al samples.



The calcined RE doped Ni-Al samples were analyzed by AAS. It shows that there is not much loss of aluminum during the preparation of catalysts.

Sample	Composition of Ni:RE:Al (mole ratio)	
	Nominal	AAS
Ni-Al	2 : 1	2.15 : 0.847
Ni-La-Al	2 : 0.1 : 0.9	2.05 : 0.095 : 0.88
Ni-Pr-Al	2 : 0.1 : 0.9	2.03 : 0.093 : 0.84
Ni-Nd-Al	2 : 0.1 : 0.9	2.01 : 0.092 : 0.83
Ni-Sm-Al	2 : 0.1 : 0.9	1.97 : 0.098 : 0.85
Ni-Gd-Al	2 : 0.1 : 0.9	2.03 : 0.097 : 0.82