

Synthesis, characterization and catalytic activity of modified-clays impregnated with Ni for methane reforming

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Recibido: 02-05-05 Aceptado: 30-11-05

Abstract

One montmorillonite, STx-1 (Texas, USA) was acid activated, aluminum pillared or La-exchanged and then impregnated with Ni. Samples combining these three treatments were also prepared. The synthesized solids were characterized by X-ray diffraction, temperature programmed desorption of cyclohexylamine to evaluate the acidity, temperature programmed oxidation to determine carbon deposits and surface area by N_2 adsorption. The catalytic activity was measured using the reforming of methane with CO_2 . In general low CO_2 conversions were obtained due to the weak thermal stability of the starting material. Ni/La-pillared and Ni/La-acid-pillared clays showed the highest activity (20 and 25%, respectively) and this was ascribed to the basic properties provided by La addition, which favor the CO_2 adsorption. A rapid deactivation of the catalysts was observed and attributed to Ni sintering.

Key words: Clays; dry reforming of methane; Ni catalysts; Pillared clays.

Síntesis, caracterización y actividad catalítica de arcillas modificadas impregnadas con Ni para la reformación de metano

Resumen

Se activó una arcilla Ca-montmorillonita (STx-1, Texas-USA) con ácido, pilareándola con aluminio o intercambiada con lantano y posteriormente impregnada con Ni. También se prepararon sólidos combinando estos tres tratamientos. Los catalizadores sintetizados fueron caracterizados por difracción de rayos-X, desorción a temperatura programada de ciclohexilamina para evaluar la acidez, oxidación a temperatura programada para determinar la formación de depósitos carbonáceos y área superficial por adsorción de N_2 . La actividad catalítica fue medida usando la reformación de metano con CO_2 . En general, se obtuvieron bajas conversiones de CO_2 debido a la débil estabilidad térmica del material de partida. Los catalizadores de Ni/LaAlPILC y Ni/La-HPILC fueron los que mostraron las actividades más

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altas (20 y 25%, respectivamente) y esto fue atribuido a las propiedades básicas promovidas por la adición de La, el cual favorece la adsorción de CO₂. Se observó una rápida desactivación de los catalizadores y esto fue atribuido a la sinterización de Ni.

Palabras clave: Arcillas; arcillas pilareadas; catalizadores de Ni; reformacion seca de metano.

Introduction

The process of carbon dioxide reforming of methane to synthesis gas has received considerable attention in recent years because of the possibility to convert two of the cheapest carbon-containing materials into useful feedstock for further chemical processes (1, 2). Another reason for this renewed interest is environmental considerations since this reaction consumes carbon dioxide and methane, both greenhouse gases. The factor leading to increased environmental interest in this process is the endothermic nature of the reaction that makes it possible to store solar energy as synthesis gas.

Supported nickel catalysts are commonly used in industrial catalytic processes such as dehydrogenation, steam reforming, and hydrogenolysis of hydrocarbons. Normally, the supports used are metal oxides or activated carbon.

Natural untreated clays possess very low ability to catalyze chemical reactions. However, the structural properties of these materials can be modified by various activation methods in order to produce catalysts with high acidity, surface area, porosity and thermal stability. Acid activation of clay minerals is one of the most effective methods used to produce active materials for adsorption and catalysis. Layered clays which are aluminosilicates, in particular montmorillonites and its pillared derivatives, have also been used for hydrogenation and dehydrogenation (3, 4). Excellent activity for selective reduction of NO catalyzed by ion-exchanged pillared clays has been observed (5); meanwhile, it is well known that the pore structure and morphology of the support

can greatly influence the catalytic activity and selectivity.

Clay minerals are interesting materials as catalyst supports, not only due to their great abundance and low cost but also to their particular properties and structure. Therefore, the aim of this work was to prepare modified acid-pillared impregnated Ni-clays, to study their textural characteristics, and to evaluate the catalytic activity of the synthesized materials towards the methane reforming reaction.

Materials and Methods

Catalysts preparation

One source clay was selected: Caumontmorillonite (STx-1, henceforth referred to hereafter as ST, dioctahedral bentonite of low iron content) Texas-USA, obtained from the Mineral Repository of the Clay Mineral Society, was used without further purification. The cation exchange capacity (CEC) of ST is 0.80 meq g-clay⁻¹ and the surface area is 75 m² g⁻¹.

Acid activated ST (HST) was obtained by adding the appropriated amount of clay to a solution containing 1.5 M HCl equivalent to 48 mmolH⁺ g-clay⁻¹. The mixture was vigorously stirred overnight at room temperature and then centrifuged, washed, dried at 120°C and ground.

ST and HST clays were pillared (PLST and HPLST) with aluminum, as follows: a solution containing the aluminum complex, prepared using the procedure reported by Bradley *et al.* (6), was added drop-wise to a 1 wt% clay suspension in constant stirring at room temperature for 2 h. The stirring was maintained for 2 h and then stopped for

1 h to allow sedimentation. The solid obtained was vacuum filtered, washed and dried at 120°C for 1 h, then calcined at 500°C, and ground.

La-pillared clays (LaPLST and HLaPLST) were prepared using a solution with a La:Al = 1.5 and a concentration of 2.5 M Al, which was added drop-wise into the clay slurry under stirring as described above. The clay aluminum ratio was 20 mmol Al g-clay⁻¹.

ST and HST were exchanged once with a solution of 0.1 M of lanthanum nitrate (LaST and HLaST), and both samples were washed until conductivity was detected (<30 μS).

All nickel catalysts were prepared by wet impregnation method with Ni loading of 5 wt% using nickel nitrate as a precursor compound. The clay support was added into a nickel solution and heated under constant stirring to evaporate water, dried at 110°C overnight and finally calcined at 500°C in air for 4h.

Catalysts characterization

The BET surface area and porosity of the prepared catalysts were measured by nitrogen adsorption isotherms at 77 K, conducted on a NOVA 1000 Quantachrome Instrument. Samples were outgassed at 120°C for 2 h before the adsorption measurements.

X-ray powder diffraction traces of the clays were recorded using a JEOL JDX diffractometer, operating at 30 kV and 30 mA at a scan speed of 2° min⁻¹ from 2 to 60° 2θ, using Cu-Kα radiation. The crystalline phases were identified using the tabulated powder diffraction files of the ICDD (International Center Diffraction Data) d-spacing files.

Temperature programmed oxidation (TPO) experiments of carbon species formed on the catalysts were carried out on a thermogravimetric analyzer (TG-DTA 2000S Material Analysis Characterization) by

passing air at a flow rate of 80 mL min⁻¹, using a heating rate of 15°C min⁻¹. The thermal desorption of cyclohexylamine was used to monitor the acidity of the prepared samples. The experimental procedure is identical to that reported elsewhere (7).

CO₂ reforming of methane over Ni catalysts was carried out at 700°C and at atmospheric pressure with a tubular fixed-bed quartz reactor. The reaction gases were CO₂ and CH₄ with a molar ratio of 1:1 at a flow rate of 100 mL min⁻¹ (GHSV = 60,000 mL g⁻¹ h⁻¹). Twenty milligrams of the catalyst were placed in the reactor and reduced *in situ* at 500°C for 3 h in a H₂ flow. The analysis of the reactants and products was performed on two on-line gas chromatographs (GCs) using nitrogen as carrier gas. One was a Shimadzu GC-4C, equipped with a flame ionization detector and a Porapak T (80-100 mesh) stainless column. The other was a Hitachi 063 with a thermal conductivity detector, equipped with a (molecular sieve 5A) stainless column (60-80 mesh).

Results and Discussion

Catalysts characterization

Figure 1 shows the XRD traces of all Ni supported catalysts prepared. As can be seen the raw clays (ST) presents a very intense peak at 5.75°, which corresponds to a d-spacing of 15 Å. High d-spacings are also obtained on fresh catalysts (Table 1). However, after calcination of the pillared-clays (supports), the d-spacings are dramatically reduced and subsequent calcination of all Ni-impregnated catalysts further decreased them. This observation indicates that the starting clay collapses its lamellar structure due to a weak thermal stability, even after the pillaring treatment or that there was not formation of the PILCs. A series of medium and weak peaks appeared in the diffractograms and were identified (using ICDD) as nickel oxide-aluminate and nickel oxide-silicate species.

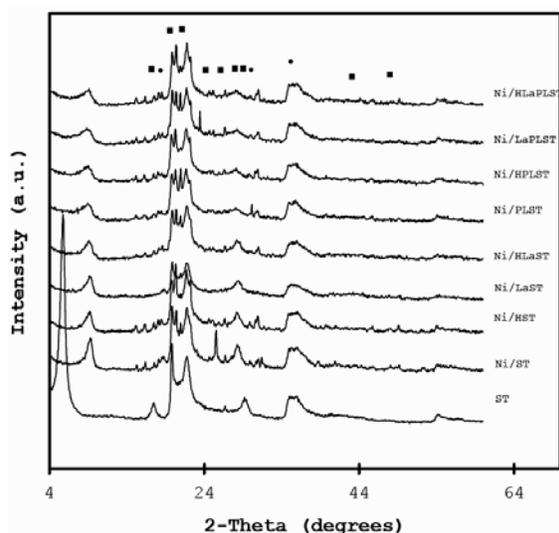


Figure 1. XRD patterns of 5 wt% Ni-impregnated clays, (■) Ni_2SiO_4 and (●) NiAl_2O_4 .

The specific surface area, total pore volume, average pore diameter and acidity of the synthesized materials are listed in Table 2. The nitrogen adsorption-desorption

isotherms (not shown) for all samples were typical of mesoporous solids (type IV isotherm using Brunauer's classification) with a clear hysteresis loop at higher P/P^0 of type B, indicating that there were no micropores but only mesopores in these solids. In general, small surface areas were obtained and these results are in line with the XRD data. The pillaring process did not increase either the surface area or the pore volume. This observation evidences a clear collapse of the lamellar structure, as stated above.

The decrease in surface area lowers the Ni dispersion with the concomitant reduction in activity (8).

Figure 2 shows the initial conversions yield of hydrogen and carbon monoxide at 700°C . The CO conversion was greater than that of H_2 which might indicate that the reverse water gas shift reaction occurred in the reaction process for the studied catalysts. The most active catalysts deactivated very quickly and negligible activities were detected after 20 min of reaction. There is no correlation between the surface area or the

Table 1
d-spacings (in Å) of the prepared catalysts.

Sample	Treatment	
	Fresh	Calcined
Clay-Pillared Supports	PLST	9.9
	HPLST	9.8
	LaPLST	13.3
	HLaPLST	9.8
Supports loaded with 5 wt% Ni	ST	15.0
	HST	16.5
	LaST	15.3
	HLaST	15.5
	PLST	9.7
	HPLST	9.2
	LaPLST	9.8
	HLaPLST	9.7

Table 2
Surface area, total pore volume, pore diameter and acidity of the catalysts

Sample	S_{BET} (m^2/g)	V_p^a (cm^3/g)	D_p (nm)	Acidity (mmol/g)
Ni/ST	47	0.117	9.76	0.33
Ni/HST	28	0.083	11.98	0.39
Ni/LaST	18	0.043	9.46	0.31
Ni/HLaST	20	0.071	14.12	0.32
Ni/PLST	31	0.048	6.16	0.41
Ni/HPLST	22	0.032	5.98	0.40
Ni/LaPLST	32	0.094	7.24	0.30
Ni/HLaPLST	26	0.042	6.56	0.26

^a Specific total pore volume at $P/P_0 = 0.98$.

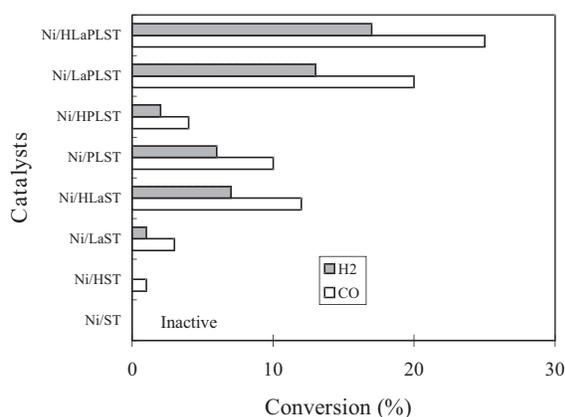


Figure 2. Initial conversions of CO and H_2 for the 5 wt% Ni loaded catalysts derived from STx-1.

pore volume with the initial catalytic activity. Some studies have demonstrated that the addition of basic promoters enhances the activity for dry reforming of methane (9, 10). In the present case, the activity is controlled by the basic properties of the catalyst produced by the incorporation of lanthanum, since the most active catalysts were Ni/LaPLST and Ni/HLaPLST which are the most basic solids (Table 1). The relatively

high acidity found in Ni/LaST catalyst is due to the exchange treatment with La, which does not completely displace Ca from the original clay. Due to the strong basicity of cyclohexylamine ($pK_b = 3.3$), it is capable to interact with both weak acid sites, like Camontmorillonites, and strong Bronsted acid sites (7). Similar findings were reported by Wang *et al.* (11), but they reported better results for the reforming of methane using a Ni supported La-pillared clays prepared by a templating method, and attributed this behavior to a greater adsorption of CO_2 by the presence of La. Additionally, the conversions observed herein are considerable smaller when compared with those obtained using conventional Ni supported on SiO_2 , Al_2O_3 or porous alumina intercalated laponite catalysts (conversions of 70-85%) (9, 12, 13).

The rapid deactivation of the most active catalyst, Ni/HLaPLST, was ascribed to sintering of Ni due to appearance of nickel peaks (at 44.2 and 51.6 θ) on the XRD pattern of the used catalyst (Figure 3). The amount of carbon deposited on the different catalysts was determined by TPO, a weight loss between 1 and 2% at 700 $^\circ C$ was observed for all catalysts. This result may indicate that the low activity of the catalysts is

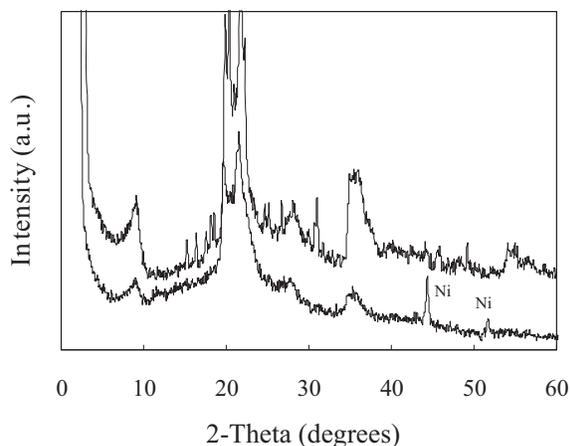


Figure 3. XRD patterns of fresh (top) and used (bottom) Ni/HLaPLST catalyst.

due to Ni sintering more than coke formation, as a direct consequence of the small surface areas obtained after calcination. Recent results (14), have revealed that Ni/MgO clay nanocomposites stabilized with surfactant are thermally stable, keeping large surface areas (e.g., $720 \text{ m}^2 \text{ g}^{-1}$) after calcinations at 500°C for 20 h, and show a high conversion of 95% for the methane reforming at 700°C .

Conclusions

The original idea of this work was to prepare catalysts of enhanced surface area produced by acid treatment, combined with good thermal stability provided by pillaring process and controlled basicity by La incorporation. However, unfortunately, no good catalytic activity results towards the methane reforming for catalysts derived from ST clay were found, and this was related to the poor thermal stability and reduced surface areas achieved, allowing small Ni dispersions and low resistance to deactivation by coke formation.

Acknowledgements

A.M. thanks The Matsumae International Foundation, Japan, for the Research Fellowship given.

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