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Kinetics of CO_2 methanation over Ce-doped Ni-Al hydrotalcite catalyst

Emanuele Giglio[1], Fabio Deorsola[1], Salvatore Abate[2], Leone Frusteri[2], Samir Bensaid[1], Raffaele Pirone[1*].

1 Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.

2 Dipartimento di Ingegneria Elettronica, Chimica e Ingegneria Industriale, Università di Messina and INSTM CASPE (Laboratory of Catalysis for Sustainable Production and Energy) - Viale F. Stagno D'Alcontres 31, 98165 Messina, Italy.

**Corresponding author: Raffaele.pirone@polito.it*

Highlights

- Chemical and physical characterization of Ce-Ni-Al hydrotalcite catalyst.
- Kinetic parameters estimation via PFR model coupled with nonlinear regression.
- Best fitting with LHHW kinetic equation based on dissociative reactants chemisorption.

1. Introduction

In the recent years carbon dioxide methanation for synthetic methane production gained a great interest. Research attention has been focused mainly on catalysts involving nickel as active compound, due to its cheap cost especially if compared with other active noble metals as ruthenium and rhodium [1]. Catalysts composed by nickel supported on several oxides have been deeply analyzed [2]; experimental investigations underlined the positive role of cerium oxide on the samples activity, as a direct consequence of the enhanced reducibility of NiO. Recently, the research attention focused also on high-loaded nickel hydrotalcite-like catalysts due to the high activity showed [3]. Nevertheless, in the open literature few studies deal with high pressure (and high reactants concentration) methanation of carbon dioxide.

In this work, a Ni-Al hydrotalcite doped with CeO_2 has been tested and compared with a standard Ni-Al hydrotalcite. The aim is the merging of two effects on the catalyst activity: the high achievable Ni load (obtainable with hydrotalcite-based catalysts) and a greater reducibility of the NiO (through the addition of ceria). The results of a methanation test campaign at high pressure are presented, with the aim of investigating the reaction kinetics over such a novel catalyst under real applicative conditions.

2. Methods

The two hydrotalcite samples (HT and NiAlCe-HT) have been characterized via temperature programmed desorption (CO-TPD) and temperature programmed reduction (H_2-TPR). A test rig has been designed in order to perform the experimental activity at high pressure (up to 30 bar). A duration test (with stoichiometric inlet mixture) was initially performed in order to evaluate the trend of methane yield over time. During the experimental campaign, the reactor has been fed with stoichiometric, H_2-excess and CO_2-excess inlet mixtures. The kinetic data set has been collected in the temperature range between 250 and 350 °C, while the total operating pressure has been varied between 15 and 25 bar. Two different kinetic models have been compared and evaluated. Firstly, a power law rate equation (considering only the reactants reaction orders) has been used. Then, a LHHW-type (Langmuir-Hinshelwood-Hougen-Watson) equation has been involved. The kinetics is integrated into an ideal plug flow reactor (PFR) model. The main algorithm deals with the minimization of the overall difference between experimental and predicted conversion via nonlinear least-squares regression.

3. Results and discussion

CO-TPD has been used for the calculation of the metal surface are (MSA): NiAlCe-HT sample presented a superior value (22 m^2/g_{cat}) than NiAl-HT (13 m^2/g_{cat}). H_2-TPR showed that the peak for NiAl-HT is shifted towards a lower temperature, implying a better reducibility.

During the duration test the hydrotalcite samples present an initial activity drop over the first 15 hours, after which the catalyst performance stabilized to an almost constant value. The initial performance drop can be attributed to morphological changes in the catalyst structure, which stabilized after a short period. Results show therefore that the tested hydrotalcite derived catalysts are characterized by a good stability over time. Activity experiments were then carried out after the stability test in order to decouple kinetic measurements from deactivation phenomena. In Figure 1 some results of the experimental investigation are presented. NiAlCe-HT presented higher activity than the standard Ni-Al hydrotalcite (HT).

Concerning the LHHW-based kinetics, the equation leading to the best fitting is based on a dissociative chemisorption of both the reactants (H_2 and CO_2). In Figure 1 a sketch of the test unit and some results of the experimental investigation are presented.

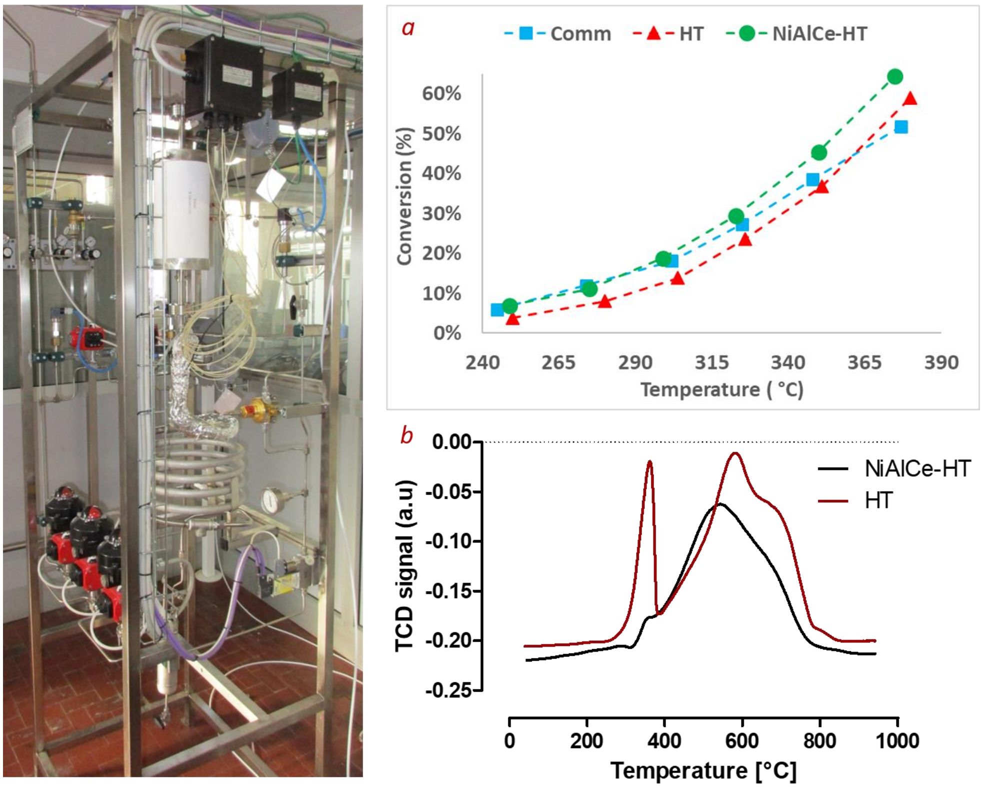

Figure 1. Comparison between the tested samples (a) and H_2-TPR pattern for the two hydrotalcites (b).

4. Conclusions

The catalysts characterization suggested that the Ce-addition seems to enhance the performance of the Ni-Al hydrotalcite, improving the MSA and the reducibility. Kinetics of carbon dioxide hydrogenation for synthetic methane production has been investigated. The experimental campaign suggested the reactants dissociative chemisorption as possible reaction scheme. The obtained intrinsic kinetics can be used for the methanation reactor modeling. Depending on the chosen reactor concept, the model should take into account the effect of internal and external transport phenomena between the gas mixture and the solid catalyst.

References

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Keywords
CO_2 methanation, intrinsic kinetics, nonlinear fitting.