



Mesoporous oxidic holey nanosheets from Zn-Cr LDH synthesized by soft chemical etching of Cr³⁺ and its application as CO₂ hydrogenation catalyst



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ARTICLE INFO

Keywords:

CO₂ hydrogenation
β-Diketonate ligands
Etching
Mesoporous nanosheet
Zn-Cr-LDH

ABSTRACT

High surface area mesoporous holey hydroxidic nanosheets were synthesized by reacting Zn-Cr-LDH with β-diketonate ligands. The different β-diketonate ligands having keto-enol tautomeric behaviour and the strength of enolic acids increasing in the order 1-phenyl-1,3-butanedione < 2,4-pentanedione < 1,1,1-trifluoro-2,4-pentanedione were reacted with Zn-Cr-LDH. Strong 1,1,1-trifluoro-2,4-pentanedione reacted with Zn-Cr-LDH at room temperature itself and broken the layered structure of LDH forming a segregated Cr³⁺ stable diketonate complex. On the other hand, 2,4-pentanedione and 1-phenyl-1,3-butanedione reacted with Zn-Cr-LDH at temperatures 45 and 65 °C respectively. 2,4-Pentanedione preferentially etched out Cr³⁺ ion by leaving behind the LDH like structure with mesoporous holes. 1-Phenyl-1,3-butanedione due to its still weaker acid strength could not etch out Cr³⁺ ion. The pores obtained in the LDH nanosheets from the reaction with 2,4-pentanedione were found within a narrow size range of 2–10 nm. Also, their BET surface area was higher. The calcined form of this mesoporous material was used as a catalyst for the hydrogenation of CO₂. The catalytic reactions carried out at temperature 200–400 °C showed approximately 100% selectivity towards CH₄ with a small amount of H₂O as a by-product without the deposition of coke and formation of additional CO. Thus, by virtue of its improved performance at lower temperatures it is expected to have an advantage over many existing similar CO₂ hydrogenation catalysts.

1. Introduction

Presently, CO₂ is considered as the most dreaded green house gas with a massive environmental threat. The CO₂ concentration in the environment has risen from a pre-industrial level of 2.8×10^{-4} ppm to a present level of 3.86×10^{-4} ppm [1–4]. Sequestration of CO₂ is considered as an immediate remedy to control its rapidly rising concentration. Another important strategy to reduce global warming is the conversion of CO₂ to valuable feedstock like methane by Sabatier reaction [3,5–7] –



Due to its high calorific value and environmental friendliness CH₄ is considered as a highly efficient future energy carrier [8]. Conversion of CO₂ to CH₄ over different transition or non-noble metal supported, various mesoporous and LDHs based catalysts has been investigated by

many researchers [1–20]. This reaction is accompanied by two side reactions one is CH₄ decomposition and another is Boudouard reaction of disproportionation of CO₂ [16]. Coke formed in these side reactions suppresses the catalytic activity [16]. Therefore, the formation of CH₄ from CO₂ by controlling such type of side reactions is one of the most important areas of research.

Different catalysts like nickel-based Ce_xZr_{1-x}O₂ catalyst, Co-Fe bimetallic catalyst, Manganese complexes, Ni-Al-LDH, W-doped Ni-Mg mixed oxide for the hydrogenation of CO₂ has been reported (Razzaq et al. [8], Gnanamani et al. [9], Rawat et al. [2], Abate et al. [17] and Yan et al. [21]). Although, all these catalysts acted positively in the methanation reactions at low temperatures but some higher hydrocarbons and some additional CO are also formed as by product due to which the selectivity towards CH₄ decreases. Also, in case of some of these catalysts the coke deposition causes further decrease of catalytic activity.

Reports are there about the use of some mesoporous catalysts which

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<http://dx.doi.org/10.1016/j.jcou.2017.06.017>

Received 20 May 2017; Accepted 24 June 2017

Available online 05 July 2017

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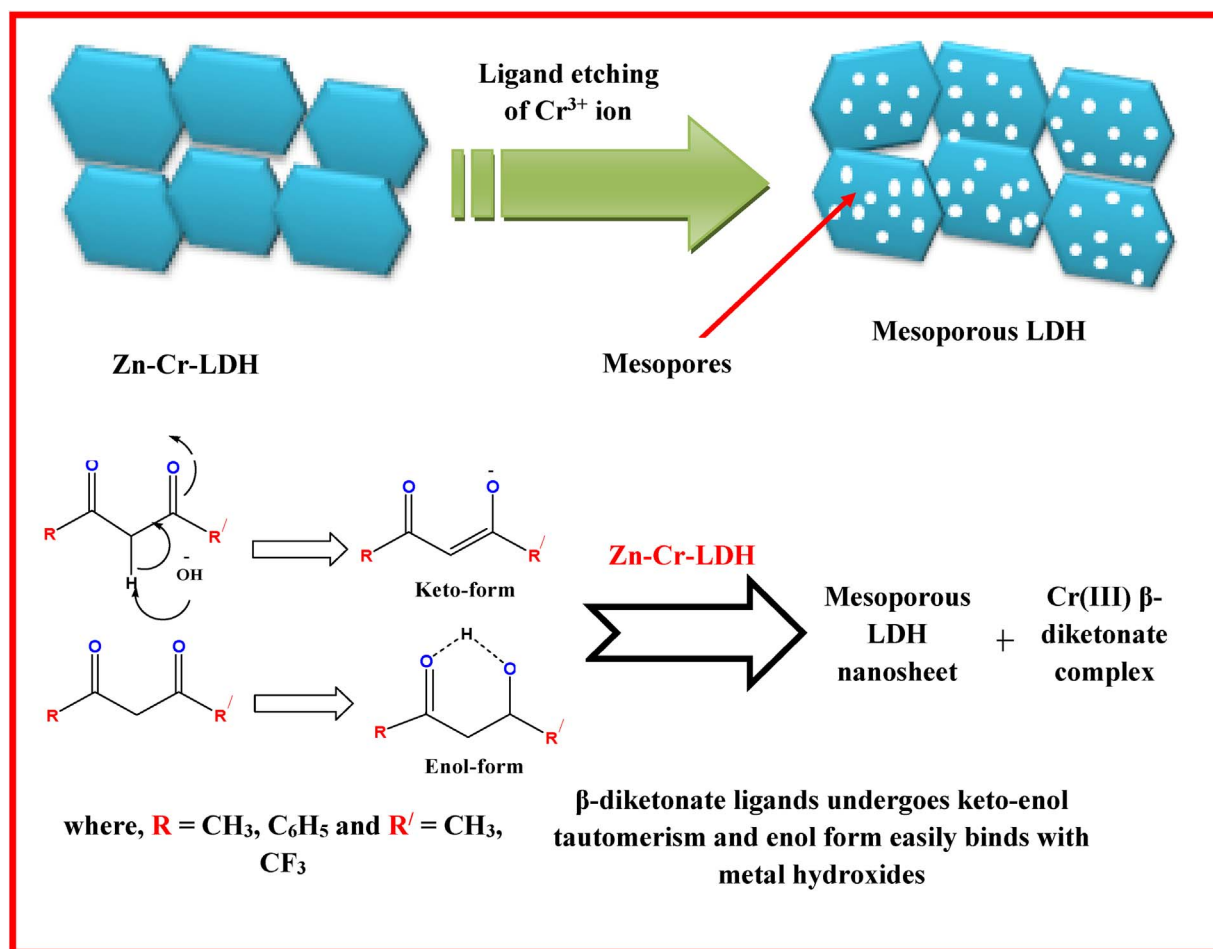


Fig. 1. Mechanism of the formation of mesoporous LDH by keto-enol tautomerism of β-diketonate ligands.

have reduced coke deposition property and high CO₂ selectivity. It is reported that, due to the high surface area, enhanced yields, selectivity and ability to control the pore structures mesoporous materials are advantageous over other catalysts (Linares et al. [22]). Xu et al. [16,23] has reported the CO₂ methanation over mesoporous CoAl₂O₄ and NiO-Al₂O₃ type mixed oxide spinels. Similarly, Nannan et al. [24] has reported about the use of mesoporous Ni-CaO-ZrO₂ based catalysts for conversion of CO₂ and CH₄ to CO and H₂ or dry reformation without any formation of carbon deposits. Apart from these, several other mesoporous catalysts for CO₂ methanation reaction like ZSM5, mesoporous Co/KIT-6 and Ni-MCM-41 catalyst are also reported (Teh et al. [13], Zhou et al. [15], Du et al. [20]). Although, these catalysts act effectively for the CO₂ methanation reaction at low temperature without deposition of coke, the hydrothermal instability of the mesoporous framework of these catalysts deactivates them easily.

In this paper, we are reporting the CO₂ methanation reaction in presence of mesoporous catalysts derived from Zn-Cr Layered Double Hydroxide (LDH) precursor. LDHs have the general formula [M_{1-x}M_x³⁺(OH)₂]^{x+}[A_{x/n}]ⁿ⁻·m H₂O where, M²⁺ = Zn²⁺, Ni²⁺, Mg²⁺, Cu²⁺ ions etc. and M³⁺ = Cr³⁺, Al³⁺, Co³⁺ ions etc. with Aⁿ⁻ as different intercalated anions [25–28]. LDHs are used in many environmentally important reactions such as control of N₂O emission, hydrogenation of CO₂, catalytic partial oxidation of CH₄ to syngas. Due to various catalytically important properties such as high surface area, uniform atomic level distribution of metal ions in the same nano-sheet, compositional diversity, acid-base bifunctionality LDH can be used to synthesise new structured and novel supported catalysts [17–19,29–38]. The use of Zn-Cr-LDH as catalyst in hydrogen production has been reported by D. et al. [39]

In this work report is made about the synthesis of mesoporous Zn-bearing-LDH like nanosheets by the interaction of Zn-Cr-LDH with some β-diketonate ligands. Generally, β-diketonate ligands are bidentate ligands which undergo keto-enol tautomerism and reacts with metal hydroxides by acid-base neutralization reactions through their enolic tautomer [40–45]. In the process in many cases with metal ions like Zn²⁺, Cr³⁺ and Cu²⁺, they also form sublimable metal β-diketonates which have important applications as Chemical Vapour Deposition film growth precursors.

The synthesis of mesoporous Co-Al-LDH by alkali etching of Al³⁺ ion was also reported by Lu et al. [46]. Radha et al. [47] have reported preferential leaching out of Cr(III) ion from Zn-Cr LDH structure by alkaline hypochlorite solution, however, the Zn(OH)₂ formed had a structure different from the parent LDH. Similar synthesis of mesoporous holey nanosheets with in plane pores from another synthetic layered material MnO₂ by selective leaching of some Mn⁴⁺ ion centers through some oxidation reduction reaction involving surface adsorbed Fe³⁺ ions has also been reported by G. Zhang et al. [48]

The method we present is a simple low cost, soft chemical method of development of holey mesoporosity in layered oxidic nanosheets and for that matter in their layered hydroxidic precursor. The method adopted here is different from the mesoporosity development in layered materials by intercalation of some active metal or metal oxide pillars inside LDH nanosheets. The present work also reports the effect of acid strength of β-diketonate ligands on their reaction with Zn-Cr-LDH. To the best of our knowledge synthesis of the mesoporous LDH by preferential etching out of constituent metal ion by some organic ligands and use of their calcined product in CO₂ hydrogenation reactions as catalyst has not been reported yet.

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