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FT-IR spectroscopic and catalytic study of de-aluminated H-mordenites as environmental friendly catalysts in the hydroxymethylation of 2-methoxyphenol with formaldehyde in aqueous medium

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Abstract

Several de-aluminated H-mordenites, prepared by treating a commercial H-mordenite (HM-16, Engelhard) with aqueous HCl solutions, were characterized and tested as catalysts in the liquid-phase hydroxymethylation of guaiacol with aqueous solutions of formalin, for the production of *p*-vanillic alcohol (3-methoxy-4-hydroxybenzyl alcohol), the intermediate in vanillin synthesis.

Samples were obtained with Si/Al atomic ratios from 10 to 36; their acidic and hydrophilic properties have been characterized by means of FT-IR spectroscopy of adsorbed probe molecules, namely CO at nominal 77 K, NH_3 and H_2O at room temperature, and ammonia TPD.

De-alumination led to the development of a mesoporous structure, and to a partial structure degradation with the most de-aluminated sample (Si/Al = 36).

As to the acidic properties, both Brønsted species in the main channels and in side-pockets were removed, and less acidic hydroxyls formed.

The catalytic performance was affected mainly by samples hydrophilicity that considerably decreased upon de-alumination. In the Si/Al ratio range investigated, a decrease in the number of acidic sites led to a complex catalytic behaviour, with a maximum activity for intermediate Si/Al ratio (=25). A higher concentration of aromatic compounds in the pores of more hydrophobic zeolites (higher Si/Al ratios) also led to a higher selectivity towards heavy, di-arylic by-products. A comparison with commercial H-mordenites having similar Si/Al ratio evidenced that the occurrence of mesoporosity, in strongly de-aluminated samples, also affected the catalytic performance, favouring the formation of bulky di-aryl compounds and leading to lower guaiacol conversion.

Keywords: Mordenite; De-alumination; Hydrophilicity/hydrophobicity; Heterogeneous catalysis; FT-IR spectroscopy; Hydroxymethylation of Guaiacol; Vanillols

1. Introduction

The synthesis of 3-methoxy-4-hydroxybenzaldehyde (vanillin), an important food additive, is currently carried out by processes with heavy environmental impact or by multi-step synthesis, in which the use of specific reactants is a drawback for the process economy. Typical examples are (i) the process starting from aniline and nitrochlorobenzene, which involves several steps and co-produces huge amounts of aqueous solutions of inorganic salts that have to be disposed; (ii) the reaction between guaiacol and glyoxylic acid, followed by oxidation and acidic hydrolysis of the adduct to generate vanillin, which suffers from the high cost of the reactant used; (iii) the process in which guaiacol hydroxymethylation in basic medium is carried out after protection of position 6 in the aromatic ring via the Kolbe reaction [1].

The development of new synthetic procedures is desirable, in order to avoid co-production of inorganic effluents, and to minimize production costs by using cheaper raw materials, and by optimizing each step to the highest selectivity to the desired

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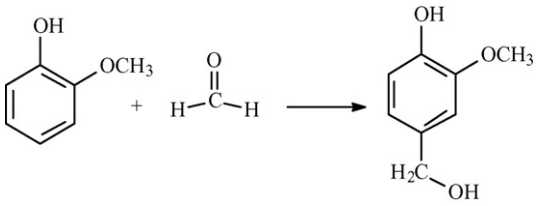


Scheme 1.

product, in order to reduce waste and by-products [2,3]. The same drawbacks occur in several liquid-phase acid catalyzed reactions for fine-chemicals and intermediates production, when Friedel–Crafts-type reactions are used for the functionalization of organic substrates. This problem can be approached by developing suitable solid catalysts with controlled acidic properties [4,5]. Several reviews have addressed this problem [6–8] and, in some cases, the successful commercialization of heterogeneously-catalyzed alkylation and acylation reactions of aromatic substrates have clearly indicated the potentialities of this approach [9].

Arylaldehydes may be produced via oxidation of arylmethanol, obtained by hydroxymethylation of the arene with formaldehyde [10–16]; the reaction can be carried out with several substrates, such as anisole, phenol and furfuryl alcohol, and other aldehydes or epoxides as well, to yield either the corresponding mono-aryl alcohol, or di-aryl derivatives [17–27]. Usually, the reaction requires the use of activated arenes (containing hydroxyl- or methoxy-functional groups), and is typically catalyzed by Brønsted acids. In the synthesis of the mono-aryl alcohol, the control of selectivity is difficult, since the alcohol produced readily reacts to yield di-aryl or poly-aryl compounds.

In the case of hydroxymethylation of 2-methoxyphenol (guaiacol) to *p*-vanillic alcohol (Scheme 1): the reaction represents one-step in the multistep, environmentally friendly process for the production of vanillin (Scheme 2) [2].

The reaction reported in Scheme 1 is catalyzed by zeolites [10,11]; since formalin, the aqueous solution of formaldehyde, is an easily available and cheap raw material, hydrophobic zeolites are needed, in order to avoid preferential filling of the pores by more polar water molecules rather than by the aromatic substrate [16].

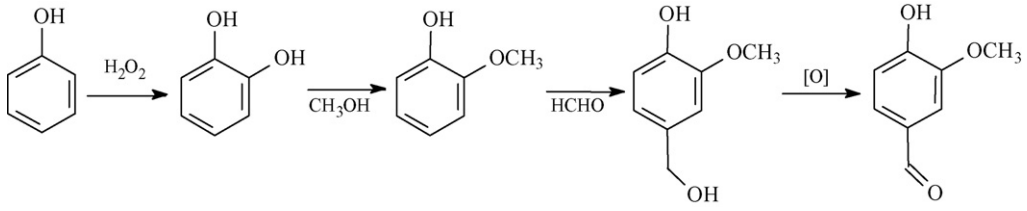
In previous studies [28–31], we have investigated the reactivity of H-mordenites in the hydroxymethylation of guaiacol, and specifically: (i) the influence of the presence of methanol in the formalin solution on catalytic performance; (ii) the role of the main reaction parameters; (iii) the scheme of reaction, and the ways to control the extent of consecutive reactions upon *p*-vanillols; (iv) the role of hydrophobic properties of three commercial H-mordenites with very different Si/Al ratios: 10, 23 and 58.

This work reports about the effect of de-alumination on the physico-chemical properties and reactivity in liquid-phase guaiacol hydroxymethylation of catalysts obtained starting from a commercial H-mordenite with Si/Al = 10. The role of zeolite properties, i.e., porosity, acidity and hydrophobicity/hydrophilicity, in a limited range of Si/Al ratio (from 10 to 36) has been investigated, in order to find out whether a procedure aimed at the control of zeolite characteristics may lead to a catalyst with improved performance in the synthesis of vanillol.

2. Experimental

Several samples have been obtained via de-alumination of a commercial sample in powder form provided by Engelhard, HM-16 (Si/Al = 10); corresponding Si/Al ratios, as checked by atomic absorption, along with some textural properties, are gathered in Table 1.

De-alumination has been performed by treating the parent sample (HM-16) in a HCl aqueous solution (HCl concentrations from 0.1 to 5 M). De-aluminated mordenites are referred to with the code D*x*, where *x* indicates the molar concentration of the acid used (Table 1). The treatment was carried out for 2 h at 373 K, with a weight ratio between the zeolite and the solution of 1:50. The zeolite was then washed with water until



Scheme 2.

Table 1
Si/Al ratio as determined by means of atomic absorption, after dissolution of samples and related textural properties

Sample	Si/Al ratio	BET ($m^2\ g^{-1}$)	ESA ($m^2\ g^{-1}$)	Micropores volume ($cm^3\ g^{-1}$)	Average mesopores diameter (Å)
HM-16	10	402	52	0.17	31
D01	13	424	66	0.19	40
D1	25	425	72	0.19	40
D2	32	431	92	0.20	40
D5	36	380	106	0.17	40

BET and external surface area (ESA) ($m^2\ g^{-1}$), micropores volumes ($cm^3\ g^{-1}$), BJH mesopores diameter (Å), as determined by means of N_2 adsorption/desorption at 77 K.