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The transformations involving methanol in the acid- and base-catalyzed gas-phase methylation of phenol

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Abstract

The alkylation of phenol with methanol was studied using a Brønsted-type acid catalyst (a H-mordenite) and basic/dehydrogenating catalysts (MgO, Fe_2O_3 and Mg/Fe/O), with the aim of investigating the reaction mechanism. The main difference between the two classes of catalysts concerned the transformations occurring on methanol. Specifically, in the former case the acid-type activation of methanol led to the development of an electrophylic species that gave rise to the formation of anisole and of *C*-alkylated compounds. With basic catalysts, methanol dehydrogenated to formaldehyde, which then underwent transformation to methylformate and to decomposition products, i.e., CO, CO_2, CH_4 and H_2. In this case, the prevailing compounds obtained by reaction with phenol were *o*-cresol and 2,6-xylenol. The dehydrogenation of methanol was found to be the key-step in the generation of the active methylating species with basic catalysts.

Keywords: Basic catalysis; Acid catalysis; Phenol methylation; Methanol dehydrogenation

1. Introduction

The methylation of phenol and phenol derivatives has been widely investigated, and several papers report about the effect of the catalyst characteristics on the nature and distribution of products. The reaction has a great relevance from the industrial point of view [1]; for instance, 2,6-xylenol is the monomer for the production of poly-(2,6-dimethyl)phenylene oxide resin; 2-methylphenol (*o*-cresol) is the monomer for the synthesis of epoxycresol novolacks; 2,5-dimethylphenol is the intermediate for the synthesis of dyes, antiseptics and antioxidants, and 2,3,6-trimethylphenol is the starting compound for the preparation of vitamin E. The products of *O*-methylation of phenol (anisole) and of diphenols (e.g., guaiacol) are intermediates in the production of skin protection agents and food additives.

Preferred alkylating agents are methanol and dimethylcarbonate, while more conventional reactants, such as methylchloride and dimethylsulfate, although still employed industrially, are nowadays less attractive due to environmental concerns [2–4].

The *C*-methylation of phenol aimed at the production of *o*-cresol or of 2,6-xylenol is industrially carried out with methanol as the alkylating agent and with catalysts possessing basic characteristics [5–13]. Catalysts are made of either (i) supported and unsupported alkali and alkaline-earth metal oxides [14–18], or (ii) transition or post-transition mixed metal oxides [19–33], or (iii) mixed oxides containing both alkaline-earth metals and transition metal ions [34–44]. They are used in prevalence for gas-phase methylation, since under liquid-phase conditions a low conversion is generally achieved. This is attributed to the lower reaction temperature, and to the stronger interaction that develops between the catalyst and phenol in the condensed phase.

The strongest basic catalysts are alkali and alkaline-earth metal oxides, which however may deactivate by interaction

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with weak acid molecules, included carbon dioxide and water. Therefore, preferred basic materials for industrial applications are transition metal oxides (e.g., supported V/Fe mixed oxides [45], or Cr oxide [46]) that are claimed to exhibit medium-strength basic properties [1,45–47]. Similar reactivity is exhibited by those mixed oxides that couple the O^{2-} nucleophilicity, typical of alkali or alkaline-earth metal oxides, with the coordinating properties of transition metal oxides [1,47–49]. One example is MgO, in which the H^+-abstracting properties are modulated through the introduction of host cations [35,44]. The addition of increasing amounts of Fe^{3+} to MgO in samples prepared by thermal decomposition of hydrotalcite-like precursors, with Mg/Fe atomic ratio between 2 and 6, lead to the formation of solid solutions having general composition $Mg_{1-x}Fe_xO_{1+0.5x}$ and medium-strength basic sites [50]. The latter derived from the higher electronegativity of Fe^{3+} as compared to Mg^{2+}, that decreased the charge density on the neighboring O^{2-} and made the latter less nucleophilic than O atoms in MgO [50].

Characteristics of catalysts possessing basic features when used as catalysts for phenol methylation are: (i) the very high regio-selectivity in *C*-methylation, since the *ortho*/*para*-methylation ratio is in all cases largely higher than 2, and (ii) the high chemo-selectivity, since the *O*/*C*-selectivity ratio, a function of the basic strength of catalysts, is, in general, very low. A selectivity to *o*-cresol + 2,6-xylenol as high as 98% is reported in many patents [1].

One major problem of the industrial process of phenol methylation is the low yield with respect to methanol, due to its decomposition; consequently, a large excess of methanol is usually fed in order to reach an acceptable per-pass conversion of phenol. Various solutions have been proposed to minimize this side reaction (see, for example, [48]), amongst which the co-feeding of water seems to be the most effective [45,49]. This aspect, however, is often forgotten in scientific literature, and only few papers take into consideration the methanol decomposition [19,34,51–53] and the transformations that occur on the alkylating alcohol. On the other hand, a wide literature demonstrates that methanol undergoes different transformations on metal oxides, depending on the catalyst surface properties [13,54,55].

In the present work we correlate the catalytic performance in the gas-phase methylation of phenol with the transformations that occur on methanol, for one acid (H-mordenite) and three basic catalysts (MgO, Fe_2O_3 and Mg/Fe mixed oxide), also possessing dehydrogenating properties. More specifically, the aim was to determine if the nature of the methylating species can be different when either acid or basic systems are used, and which implications this may have on the catalytic performance in phenol methylation.

2. Experimental

Fe/O, Mg/Fe/O and Mg/O catalysts were prepared by precipitation from an aqueous solution containing the corresponding metal nitrates. For instance, to obtain 15 g of MgO, 96.15 g of $Mg(NO_3)_2 \cdot 6H_2O$ (Carlo Erba Reagenti, 99% purity) were dissolved in 375 ml of distilled water. The solution was dropwise added to another solution containing 39.75 g of Na_2CO_3 (Carlo Erba Reagenti) dissolved in 375 ml of distilled water. While adding the first solution to the second one, the pH was continuously adjusted, in order to keep it close to 10.0. Under these conditions the precipitation of $Mg(OH)_2$ occurred. The so obtained slurry was left under stirring for 40 min; then the precipitate was separated from the liquid by filtration, and washed with 6 L of distilled water at 40 °C. The solid was then dried at 110 °C overnight, and calcined at 450 °C for 8 h in air. The preparation of Fe_2O_3 was carried out with the same procedure, using $Fe(NO_3)_3 \cdot 9H_2O$ (Carlo Erba Reagenti) as starting material. The same protocol was also used for the preparation of the Mg/Fe mixed oxide, using the corresponding amount of the two salts to obtain the desired atomic ratio between components.

The acid catalyst was a commercial H-mordenite, having an atomic Si/Al ratio equal to 20, shaped in 1/16″ extrudates (binder alumina). This sample was supplied by Süd-Chemie AG.

The XRD powder patterns of the catalysts were taken with Ni-filtered Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator. Surface area was measured by means of the BET single-point method (N_2 adsorption at the temperature of liquid N_2), using a Sorpty 1750 Fisons Instrument.

Temperature-programmed-reaction tests were performed with a TPDRO 1100 ThermoQuest Instruments, by saturation of a He stream with methanol at 6 °C, and feeding the gaseous stream continuously to the reactor, while heating the catalyst from 200 to 450 °C (heating rate: 10 °C/min). The effluents were analyzed by means of a VG quadrupole. The intensity of the following ion current signals were recorded: H_2 ($m/z = 2$), H_2O (18), CO (28), CO_2 (44), CH_3OH ($31 > 32 > 29 \gg 30$), CH_4 (16), HCOOH (46), CH_3OCOH (60) and H_2CO ($29 > 30 > 28$). The most intense m/z signals of formaldehyde (29 and 30) are also typical of methanol; therefore, the pressure of H_2CO was extrapolated from the comparison of the intensity profiles for signals at $m/z = 29$ and 30, with that one of $m/z = 31$.

Catalytic tests were carried out by vaporization of a methanol/phenol liquid mixture (methanol/phenol molar ratio: 10/1; liquid flow: 0.0061 ml/min; phenol supplied by Sigma Aldrich, 99+% purity; methanol supplied by Carlo Erba Reagenti) in a N_2 stream (gas flow: 20 N ml/min). The composition of the feed gas was the following (molar fractions): methanol 0.108, phenol 0.011, nitrogen 0.881. Overall gas residence time was 2.68 s. Total pressure was atmospheric. A high methanol/phenol feed ratio (10/1) was used in order to better evidence the parallel reactions occurring on methanol, (i) dehydrogenation and decomposition with basic catalysts, and (ii) formation of alkylaromatics with zeolites. Some tests were also made with a methanol/phenol feed ratio equal to 5/1. For tests made in absence of phenol, the inlet stream of methanol was maintained the same as that one used in phenol methylation tests.

The gas/vapors stream was fed to a stainless steel reactor (length: 30 cm, internal diameter: 3/4″), containing 1 cm^3 of catalyst (catalyst weight: Mg/O 0.85 g, Mg/Fe/O 0.95 g,