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Study on reuse of metal oxide-promoted sulphated zirconia in acylation reactions

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ABSTRACT

A series of sulphated zirconia samples (SZ) promoted with Al_2O_3, Ga_2O_3, and Fe_2O_3 were synthesized by co-precipitation at constant pH and aged under reflux conditions. Structural, surface and catalytic properties of the samples were investigated using N_2 adsorption/desorption, thermal analysis, *in-situ* FTIR spectroscopy, TPR–MS and EGA–MS measurements. The catalytic performance of promoted SZ in anisole acylation has been investigated. Promotion by either Fe_2O_3 or Ga_2O_3 was found to increase the catalytic activity (yield) after recycle of catalysts with respect un-promoted sample, whereas promotion by Al_2O_3 was observed to increase the conversion but not the yield. It is worth noting that all systems present high selectivity to the *p*-metoxyacetophenone product.

1. Introduction

Liquid-phase reactions, such as Friedel-Crafts acylation [1], are important unit processes for the preparation of many industrially valuable chemicals.

In recent years, increasing restrictions related to the use of traditional stoichiometric and conventional homogenous catalytic processes have been introduced because of their inherent problems such as cost, separation, handling, waste disposal, etc. [2]. Friedel-Crafts acylation is usually catalyzed by Lewis acids ($AlCl_3$, $FeCl_3$, BF_3 ...) or Brønsted acids (HF, H_2SO_4 ...). Their replacement by heterogeneous catalysts is a research topic of high interest [3–5]. Modern processes are, in fact, based on solid acids. Rhodia company (Courebevoie Cedex France), for example, is operating an industrial process for the acylation of anisole to para-acetylanisole using a zeolite-like catalyst [6]. This fixed-bed technology process is a breakthrough in the field, as it enables a considerable simplification of the process, an increase in para selectivity, and thus a reduction of the operating costs and a dramatic reduction of effluent volume. The principles of this process have been extended to the production of acetoveratrole [7]. The main drawback related to the use of zeolites is their deactivation, due to a consecutive reaction of the product with either reagents or other product molecules to form heavy by-products that remain on the catalyst [8,9]. By-products can also block the accessibility of the reactants to the catalyst micropores. In this context, sulphated zirconia (SZ) could be a better catalyst than zeolites in such reactions, due to its mesopores system which could avoid deactivation.

Recently, Jana [10] reported a new type of catalysts for Friedel-Crafts benzylation reaction. These novel red-ox metal-containing solid catalysts are very active/selective in the benzylation process.

In the present study, acylation of anisole with acetic anhydride has been investigated over Al-, Ga- and Fe-promoted SZ catalysts, and compared with unpromoted SZ systems.

Aim of this contribution is to investigate the influence of the promoters on the catalytic performances of the materials and in their possible reuse after regeneration.

2. Experimental

2.1. Catalysts synthesis

SZ samples doped with M^{3+}-oxides were synthesized by a precipitation method at constant pH, as reported elsewhere [11,12]. Briefly, a solution containing the metal cations (ZrO^{2+}

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Table 1
N2 physisorption and sulphates concentration data for all samples

Sample label	Surface area BET (m^2/g)		Pore volume (cm^3/g)	SO_4 wt.%		SO_4/nm^2	
	Fresh	After regeneration	Fresh	Fresh	After regeneration	Fresh	After regeneration
SZ	118	106	0.17	4.0	3.3	2.1_2	1.9_5
SZA	104	93	0.20	4.3	3.6	2.5_9	2.4_2
SZG	125	112	0.17	4.1	3.3	2.0_6	1.8_5
SZF	144	128	0.26	4.8	4.0	2.0_8	1.9_6

$ZrOCl_2·8H_2O$ (Fluka>+98%) and a dosed amount (3 mol%) of the other metal ion, Al^{3+}, Ga^{3+}, or Fe^{3+}) ($M(NO_3)_3·9H_2O$ (Aldrich +98%), was added dropwise under stirring to a fixed volume of water basified at pH 8 with a concentrated ammonia solution. As the precipitation of metal hydroxides tends to cause a pH dropping down, the addition of ammonia is useful to keep it constant within the range of ±0.2 pH units during the entire precipitation step.

Precipitated hydroxides were stirred for 30 min and subsequently aged for 42 h at 90 °C under reflux conditions [13–15]. Aged hydroxides were washed with water until free from chloride ions (negative $AgNO_3$ test) and dried at 110 °C for 20 h. Dried hydroxides were impregnated with a $(NH_4)_2SO_4$ solution by the incipient wetness method, to give a nominal 8 wt.% $SO_4^{=}$, and dried again at 110 °C for 20 h. Sulphated hydroxides were finally calcined at 650 °C in flowing air for 3 h. (see Table 1).

Four catalysts were prepared and they were labelled SZM, where SZ stands for sulphated zirconia, and M indicates the doping metal (Al^{3+}, Ga^{3+}, Fe^{3+}). For instance, the zirconia catalyst doped with Al_2O_3, impregnated and calcined, is referred to as SZA.

2.2. Catalysts characterization

Surface area and pore size distribution were obtained from N_2 adsorption/desorption isotherms at −196 °C (Micromeritics ASAP 2010 Analyser). Surface area was calculated by the BET equation [16]. Pore size distribution curves were determined by the BJH method applied to the adsorption isotherm branch [17].

X-ray powder diffraction patterns were measured on a Philips PW 1820/00 diffractometer, equipped with a diffracted-beam graphite monochromator, using the CuKα radiation from a sealed X-ray tube.

TPR experiments were carried out in a home-made apparatus with a 5% H_2/Ar gas mixture (40 cc/min). H_2 uptake was monitored by a Gow-Mac thermal conductivity detector (TCD), interfaced to a computer for data collection and analysis. To prevent H_2O interference in the TCD, a $Mg(ClO_4)_2$ trap was placed after the TPR reactor and before the TCD. In a typical experiment carried out on standard specimens calcined at 650 °C, a 100 mg sample was loaded in a quartz reactor and was flushed with a mixture of H_2 (5%) in Ar at temperatures up to 700 °C, with a ramp of 10 °C/min. Samples were not pre-treated before TPR tests.

Gases evolving from the TPR reactor were analyzed by a Genesys 422 quadrupole mass analyzer (QMS) by a heated capillary. The signals for m/z 34 (H_2S) and 64 (SO_2) were recorded.

Sulphate content was determined by a well-established ion chromatographic method [18].

In-situ FTIR spectra were obtained on a Bruker 113v spectrophotometer (2 cm^{-1} resolution, MCT detector). SZ systems were inspected in the form of thin-layer depositions on a Si platelet (from aqueous suspensions) to obtain information about the powders themselves. FTIR spectra of probe molecules adsorbed thereon were also run, in order to obtain information on surface acidity. Before spectroscopic experiments, all samples were activated in controlled atmosphere at 400 °C in quartz cells (equipped with KBr windows) connected to a conventional high-vacuum line, equipped with coupled rotary and turbomolecular pumps (residual pressure $p < 10^{-5}$ Torr).

2.3. Catalytic tests

The acylation reaction was carried out at 30 °C in a stirred batch reactor with a large excess of aromatic substrate (anisole 10 ml) with respect to both acetic anhydride (278 μl) and catalyst (200 mg). The intra-particle (*i.e.*, pore diffusion) and the external mass transfer effects were avoided by using the catalyst in fine powder form and by employing high stirring speed, respectively.

Before reaction all catalysts were activated at 450 °C in air for 90 min. Gases evolving from the activation reactor were analyzed with the QMS apparatus. The signals for m/z 18 (H_2O), 44 (CO_2), and 64 (SO_2) were recorded.

Upon addition of the reactants, the catalyst (originally white) became pale orange in the colorless solution and deepened to brown-red with reaction time.

Small amounts (100 μl) of the reaction mixture were analyzed after 10, 20, 30, 60, 120 and 180 min by an HP-6890 gas chromatograph equipped with an HP-5 column and a FID detector. GC–MS measurements were performed in order to recognize the metoxyacetophenone isomers and the by-products.

After 3 h the reaction mixture was quickly cooled down, separated from the catalyst, washed with anisole dried at 110 °C and kept for re-usability tests. Exhausted samples were reactivated in air at 450 °C in flowing air. In order to study the carbonaceous species deposited on the catalysts, gases evolving from the reactivation reactor were analyzed with the QMS apparatus. The signals for m/z 18 (H_2O), 43 ($(CH_3CO)O$), 44 (CO_2), 45 (CH_3COOH), and 64 (SO_2) were recorded.

Conversion at time t is calculated on the consumed acetic anhydride (AN_0 represents the initial conversion, whereas AN represents the conversion at time t, and C is referred to the concentration of both species):

$$\text{conversion}\,\% = \frac{C_{AN_0} - C_{AN}}{C_{AN_0}}100$$

whereas yield is based on the produced metoxyacetophenones (MAP):

$$\text{yield}\,\% = \frac{C_{MAP}}{C_{AN_0}}100$$

3. Results and discussion

N_2 adsorption/desorption isotherms of all samples are of IV type of the BDDT classification [19], and are characteristic of well-developed mesoporous systems. Hysteresis loops are all of H2–H3 types (see Fig. 1). Mesopores size distribution curves indicate that all samples exhibit a unimodal Gaussian-shaped pore size distribution. BET and BJH characterization data are collected in Table 1. SZA exhibits the smallest specific surface area (SSA), whereas SZF shows the highest SSA and total pore volume. The other samples exhibit a similar (and lower) pore volume.