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Modification of acid–base properties of alkali metals containing catalysts by the application of various supports

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Abstract

Four different supports, SiO_2, Al_2O_3 and Nb_2O_5 (hydrated and dehydrated) were impregnated with alkali metal acetates to obtain alkali-modified materials. The textural parameters of the samples were estimated on the basis of XRD and IR measurements and nitrogen adsorption/desorption method. The acid–base properties of the obtained materials were tested in the cyclisation of acetonylacetone and decomposition of 2-propanol. Moreover, the prepared catalysts were used in the sulphurisation of methanol towards methanethiol and dimethyl sulphide production, which appeared a well-tested reaction and exhibits the commercial aspect—environmentally friendly production of thiol. The modification of both niobia supports with alkali metal species creates acid–base catalysts highly selective in the methanethiol production, whereas the impregnation of silica and alumina with these species leads to the generation of basicity.

Keywords: Silica; Alumina; Niobia; Alkali metal modification; 2-Propanol decomposition; Acetonylacetone cyclisation; Methanol sulphurisation

1. Introduction

Industrial chemistry in the new millennium is widely adopting the concept of "green chemistry" to meet the fundamental scientific challenges of protecting human health and environment while simultaneously achieving commercial profitability. One of the approaches for obtaining this target is to explore alternative reaction conditions and reaction media to accomplish the desired chemical transformations with minimal by-products or waste, as well as eliminating the use of conventional organic solvents, if possible. Some of the important alternative tools include the use of heterogeneous catalysts instead of the traditional homogeneous systems. The heterogeneous catalysis is becoming even more important for establishing lower cost and environmentally clean processes. Therefore, basic solid catalysts have been used to perform, efficiently and in the absence of solvent, a series of fine chemistry reactions [1,2].

In the literature, one can find the description of various catalysts exhibiting basic properties, mainly based on alkali metals supported on matrix having high surface area. Many studies have been done on zeolites modified with alkali metal cations (e.g. [3–16]). Most of the papers dealing with generation of basic properties in zeolites and mesoporous molecular sieves describe the effects of cesium loading (e.g. [7]). Moreover, many papers are devoted to studies of acidic–basic properties of various oxides, mixed oxides and doped oxides. Among them the most often studied are alumina (e.g. [17–22]), magnesia (e.g. [17,20,22–24]), zirconia (e.g. [17,19]), ceria (e.g. [17]), silica (e.g. [22]), niobia (e.g. [25]) and gallium oxide (e.g. [19]). However, there are less systematic studies of these metal oxides modified with all alkali metal elements. The role of alkali metal oxides loaded on the surface of such oxide supports can be the diminishing of the support acidity and the creation of their own basicity or Lewis acidity if alkali metal occupies the cationic position which compensates the network charge (the latter case mainly occurs when zeolites are applied as the supports). Taking that into account one should consider both acidity and basicity of the metal oxides modified with the alkali metal elements, because both are changed in the final sample resulting from the modification procedure. Therefore, there is a need for the

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application of proper techniques for the evaluation of both acidic and basic properties of the catalyst surfaces. One of the methods for this purpose is the application of model reactions (e.g. [17]). The most popular model reaction seems to be the decomposition of 2-propanol. However, the commonly used interpretation that dehydration towards propene occurs on acidic sites and dehydrogenation to acetone requires the presence of basic sites is oversimplified. As Auroux and co-workers [26] mentioned the presence of pairs, Lewis basic and acidic centres on the catalyst surface leads to the inter-molecular dehydration towards di-isopropyl ether. The production of ether decreases the selectivity to acetone and it does not allow the estimation of the acid–base selectivity ratios. Therefore, this test reaction cannot be used as the only one for the characterisation of acid–base properties of the catalysts. In this work, we applied two more model reactions, not often used, for the characterisation of acid–base behavior of the solids, cyclisation of acetonylacetone and sulphurisation of methanol. It is noteworthy that hydrosulphurisation of methanol towards methanethiol is not only a well-tested reaction but it is also important for industrially thiol production (in the area of fine chemical production).

In this work, we have prepared the catalysts containing all alkali metals (from Li to Cs) located in simple oxide matrices. The advantage of such matrices is their accessibility (relatively low price) as well as the elimination of possible location of alkali metals in the form of cations playing the role of Lewis acid sites (as in the case of extra framework cations in zeolites, which block the access to the base centres). The aim of this study was the evaluation of acid–base catalytic activity of alkali metal containing catalysts basing on the matrices which exhibit various chemical composition, textural and surface properties. Amorphous silica, γ-alumina and hydrated as well as dehydrated niobia were applied as supports for alkali metals introduced to the solids via incipient wetness impregnation. The main reason for such a choice of the oxide supports was their different acidities changing from an acidic niobia, by an amphoteric alumina to non-acidic or weakly acidic silica.

2. Experimental

2.1. The catalysts preparation

Acetates of alkaline metals (Li, Na, K, Rb or Cs) were deposited onto SiO_2 (Ventron, 365 m^2/g), Al_2O_3 (Sasol, 190 m^2/g) and $Nb_2O_5{\cdot}nH_2O$ (CBMM, Brazil, 30 m^2/g) by the incipient wetness impregnation method to prepare three series of catalysts. The outgassed SiO_2, Al_2O_3 and $Nb_2O_5{\cdot}nH_2O$ (373 K, 2 h in the oven) were filled in with the appropriate amount of an aqueous solution of acetate (CH_3COOLi, CH_3COONa, CH_3COOK, CH_3COORb or CH_3COOCs, Aldrich, a volume of the solution ideally equal to the pore volume of the support) and located in an evaporator flask, where the catalyst was rotated and heated at 373 K for 1 h. The impregnated powder was dried at 373 K for 18 h and then calcined at 773 K for 10 h in an oven. In such a case, we obtained three series of catalysts: X/SiO_2, X/Al_2O_3 and $X/Nb_2O_5{\cdot}nH_2O$ (X = Li, Na, K, Rb, or Cs, respectively).

The fourth series of catalysts (X/Nb_2O_5, X = Li, Na, K, Rb, or Cs, respectively) was prepared using $Nb_2O_5{\cdot}nH_2O$ as a support but after a different pre-treatment. $Nb_2O_5{\cdot}nH_2O$ was dried at 373 K for 5 h and then calcined at 773 K for 10 h in the oven and in the presence of an air flow during 6 h. The calcined support, denoted as Nb_2O_5, was filled in with the appropriate amount of an aqueous solution of the alkaline acetates and located in an evaporator flask, where the catalyst was rotated and heated at 373 K for 1 h. The impregnated powder was dried at 373 K for 18 h and then calcined again at 773 K for 10 h in the oven.

The amount of alkali metal acetate used for the impregnation was calculated for the loading of metal equal to 0.5 mmol per 1 g of the support. Because the surface area of the modified materials differs from that of the parent one, the mole number of alkali metal cation calculated per $m^2\,g^{-1}$ is not the same for all cations located on the desired support (Table 1).

2.2. Characterisation of the materials

The texture of the catalysts was characterised using XRD, N_2 adsorption/desorption and infrared spectroscopy in the skeleton vibration region.

The XRD measurements were carried out with a Seifert C-3000 diffractometer with Cu Kα radiation (λ = 0.154 nm).

The N_2 adsorption/desorption isotherms were obtained in a Micromeritics ASAP equipment, model 2010. The samples were pre-treated in situ under vacuum at 573 K for 3 h. The surface area was calculated by the BET method. The pore size distributions (PSD), the pore sizes (the maximum of the PSD) and the mesopore volumes were determined from the adsorption/desorption isotherms using a BJH corrected algorithm.

The infrared spectra were recorded with the Vector 22 (Bruker) spectrometer. The pressed wafers of some of the materials were placed in the vacuum cell and activated at 673 K, 2 h prior to methanol adsorption at RT followed by heating at 623 K. All spectra were recorded at RT. Moreover, the spectra of all the materials (1 mg) pressed with KBr (200 mg) were registered.

2.3. Catalytic tests

2.3.1. 2-Propanol decomposition

The 2-propanol conversion (dehydration and dehydrogenation) was performed, using a microcatalytic pulse reactor inserted between the sample inlet and the column of a CHROM-5 chromatograph. The catalyst bed (0.02 g with a size fraction of $0.5\ \text{mm} < \varnothing < 1\ \text{mm}$) was first activated at 673 K for 2 h under helium flow (40 $cm^3\,min^{-1}$). The 2-propanol (Aldrich) conversion was studied at 523 and 573 K using 5 μl pulses of alcohol under helium flow (40 $cm^3\,min^{-1}$). The reactant and reaction products: propene, 2-propanone (acetone) and di-isopropyl ether were analysed using CHROM-5 gas chromatograph on line with microreactor. The reaction mixture was separated on 2 m column filled with Carbowax 400 (80–100 mesh) at 338 K in helium flow (40 $cm^3\,min^{-1}$) and detected by TCD.