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Chemical trapping studies to the determination of surface species under reaction conditions for the catalytic side-chain oxidative alkylation of toluene by methane

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ABSTRACT

MgO and MgO-modified with Na and Cs ions have been studied for the side-chain oxidative methylation of toluene with methane to C_8 fraction (ethylbenzene + styrene). The addition of two ions, rather than just only one, onto the magnesium oxide surface increases greatly the activity/productivity in this reaction and this improvement is directly connected with the high concentration of strong monoelectron-donor properties of 1% Na^+ + 1% Cs^+/MgO (4.6 [a.u. $NB^{\dot{-}}$]/m^2) studied by EPR. Chemical trapping has been a very useful technique to identify the adsorbed species on the catalyst surface under the reaction conditions. By this method, methyl and benzyl groups and epoxydating oxygen have been identified. The pre-oxidation of the surface is of paramount importance for the activation of methane and toluene. Chemical trapping and catalysts strong monoelectron-donor studies are very good experimental evidence of the radical mechanism in this reaction.

1. Introduction

Methane has been identified to be the most destructive greenhouse gas [1]. Natural gas, with CH_4 as the principal component, is mainly consumed for heating, power generation or methanol synthesis. However, in the near future, many chemicals may be produced from this natural resource. Considerable interest is presently shown in the conversion of methane to transportable liquid fuels and chemicals of importance to petrochemical industry. One problem with methane conversion is the stability of the methane molecule, with C–H bond energy of 439 kJ/mol, which makes it resistant to many reactants.

One possible new route for the utilization of methane derived from natural gas or other sources for conversion to more valuable higher hydrocarbons is the methylation of alkylaromatic hydrocarbons. Oxidative methylation of toluene with methane (OMTM) has a practical potential as a method of chemical conversion of natural gas. Products of this reaction: styrene (ST) and ethylbenzene (EB) are important compounds in the polymer industry.

OMTM process was discovered by Khcheyan et al. [2–4] and this route has been the subject of many investigations. For instance, in the direct oxidative methylation of toluene catalysts containing Fe, Co, Ni, Ti, V, Bi, Mo, Zn have been applied as the responsible active center in this reaction [3]. Yakowich et al. [5] used KBr supported on SiO_2 and obtained good selectivity towards EB and ST. Researchers, due to the similarity in the mechanism of both reactions, have tried catalysts in OMTM which are active in the oxidative coupling of methane to C_{2+} hydrocarbons. In the last 10 years, the use of basic zeolites has been observed [6–10]. Very promising yield (approx. 25%) of the C_8 fraction (EB + ST) was obtained in the presence of metal oxides with basic properties [11,12].

To synthesize better selective catalysts which could improve the C_8 fraction yield (EB + ST) and reduce the operational temperature of the process (>700 °C), we need to understand properly the mechanism according to which the reaction takes place. Khcheyana et al. [3] proposed the hypothesis in which benzyl and methyl radicals are intermediates in this reaction. Otsuka et al. [13] studied the kinetics of OMTM in presence of $LiCl/Co_3O_4$ as catalyst. In their studies, Otsuka et al. confirmed the previous hypothesis and proposed the mechanism of OMTM without convincing experimental results. According to this mechanism, in the presence of a catalyst and an appropriate amount of oxygen, benzyl and methyl radicals can be formed on the catalyst's surface by abstraction of a hydrogen atom and their consecutive coupling forms a new C–C bond of EB

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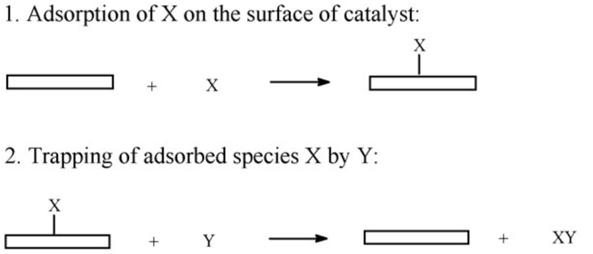

Scheme 1. Concept of chemical trapping.

which in the next step dehydrogenates to ST. Benzene is produced by cleavage of C–C bond of benzyl radicals.

Our previous investigations indicated that magnesia doped with alkali metal cations was an active catalyst in oxidative methylation of toluene and other alkylaromatic/aromatic compounds [14]. Carrying out the oxidative methylation in the flow system, for a very stable benzene molecule, 31% conversion and >14% yield of alkylation's products were obtained [14]. Our results concerning alkylaromatic side-chain methylation are in agreement with those obtained earlier by a Japanese scientific group [15,16]. However, up to date the mechanism of the reaction has not been completely determined. There are some mechanism proposals in the literature [13,17]; nevertheless, there is a lack of complete evidence for the described reaction pathways. This is probably due to the fact that reactions were carried out at temperatures different from those under which physicochemical characterization of catalyst surfaces was performed.

Chemical trapping is a method used to determine the nature of species adsorbed on catalyst surfaces, discovered and developed by Deluzarche et al. [18,19]. The essence of this method is the reaction of adsorbed species (X) with trapping agent (Y), in which an appropriate compound is formed (XY, Scheme 1). The easy identification of XY compound by GC–MS allowed us to determine the adsorbed species –X structure.

To our best knowledge, so far chemical trapping has never been used as a technique to explore the mechanism of OMTM process. The aim of this work was the recognition of the structure of adsorbed species formed on the catalyst surface by chemical trapping during the oxidative methylation of toluene with methane (OMTM) under well known catalytic systems consisting of alkali metal/alkaline earth metal.

2. Experimental

2.1. Chemical reagents and substrates

All the reactants used in this work were purchased from either Aldrich (Analytical-grade) or from POCh (Analytical-grade, Gliwice, Poland). All of these chemicals were used as received without further purification.

2.2. Catalyst preparation

The catalyst support was magnesium oxide, prepared from magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, Aldrich) by precipitation (pH 11) to $Mg(OH)_2$ using 25%-ammonia solution (Aldrich), washing 5 times with distilled water, filtration, drying at 120 °C for 3 h in ambient air and thermal decomposition at 900 °C (heating rate, 10 °C/min) for 2 h in the flow of dry air (20 mL/min). Sodium and cesium cations were introduced onto the surface from the aqueous solutions of corresponding nitrates by incipient dry impregnation in 2 mol%, respectively and by the same procedure two cations (1 mol% Na^+ + 1 mol% Cs^+) were added simultaneously onto MgO. Before the reaction, catalysts were calcined in dry air at 900 °C (heating rate, 10 °C/min) and cooled down to the reaction's temperature (750 °C).

2.3. Catalyst characterization

2.3.1. Textural properties

BET surface areas were determined using the commercial Quantasorb Junior (Model QSJR-2) unit. After outgasing at 300 °C for 1.5 h, at least two cycles of nitrogen adsorption–desorption in the flow mode were employed to determine total surface area using the standard single point BET method.

2.3.2. Strong monoelectron-donor properties (SMEDP) studies

The studies of strong monoelectron-donor properties (SMEDP) are based on Flockhart's method [20] by adsorption of nitrobenzene onto the surface of the catalyst and registration of the spectrum of the originated nitrobenzene's anion-radicals by electron paramagnetic resonance spectroscopy (EPR). In this method, the EPR's signals coming from $NB^{\overset{\cdot}{-}}$ anion-radicals formed after the adsorption of nitrobenzene on very strong monoelectron-donor surface centers of the catalyst are proportional to the surface concentration of these anion-radicals. Nitrobenzene, due to its very low electron affinity (E_A = 0.7 eV), can only be chemically adsorbed by centers with strong monoelectron-donor properties [21].

2.3.3. EPR's measurements

0.2 g of the catalyst (calcined at 900 °C for 3 h in dry air and then in a flow of dry and deoxygenated argon at 600 °C for 60 min) was inserted in a glass tube (i.d. = 4 mm, l = 25 cm) (all operations were carried out in oxygen free conditions).

The catalyst was mixed with a solution of nitrobenzene in benzene (10^{-3} M).

The glass tube was introduced in a liquid-nitrogen bath, degassed up to 10^{-2} T and sealed under vacuum.

EPR's spectra were recorded at room temperature using a Brooker ESP 300 E working in the X band with 100 kHz modulation.

The concentration of nitrobenzene anion-radicals (intensities of the EPR signals) was calculated by comparison with the intensity of the EPR signals from the DPPH (2,2-diphenyl-1-picrylhydrazyl) standard.

2.4. Catalytic tests

The oxidative side-chain methylation of toluene to C_8 fraction (EB + ST) was carried out in a vertically mounted continuous flow fixed-bed reactor at atmospheric pressure. Each catalyst (1 g) was supported on quartz wool and a layer of grain quartz (250–500 μm) above the catalyst bed served as a heating zone, ensuring that the reactants reached the reaction temperature before contacting the catalyst. The catalyst was charged into a tubular quartz reactor (i.d. = 18 mm, l = 200 mm), and then activated with a stream of dry air (20 mL/min) at 900 °C for 3 h (heating rate, 10 °C/min). Toluene (52.2 mmol/h g_{cat}) was sufficiently vaporized and fed into the reactor using a Model 100 (kd Scientific) microprocessor controlled infusion pump. The catalytic reaction was carried out at 750 °C and the molar ratio of reagents was toluene:CH_4:air = 1:12:12. Isothermal operation was maintained by diluting the catalyst bed with ground quartz (75–150 μm); the ground quartz was mixed thoroughly with catalyst before insertion into the reactor. It is generally true that laboratory scale fixed-bed reactors approximate plug flow pattern [22]. In this case, the ratio of reactor diameter to the catalyst particle (=50) exceeded the lower limit of 10 set by Froment and Bischoff [23], satisfying the application of plug-flow conditions. The reactor effluent was frozen in a dry ice-acetone trap for subsequent analysis by GC–MS (Hewlett Packard GC-6890/MSD-5973,