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

Juan Carlos Colmenares [a,b,*], Jacek Kijenski [c], Enzo B. Arévalo-García [d]

[a] Loker Hydrocarbon Research Institute, USC, 837 Bloom Walk, Los Angeles, CA 90089-1661, USA
[b] Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01224 Warsaw, Poland
[c] Industrial Chemistry Research Institute, ul. Rydygiera 8, 01793 Warsaw, Poland
[d] Department of Chemistry, CW Post L.I.U., Long Island, NY 11548, USA

ARTICLE INFO

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. $NB^{\ominus}$]/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.

© 2009 Elsevier B.V. All rights reserved.

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
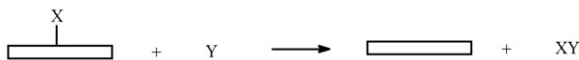
1. Adsorption of X on the surface of catalyst:
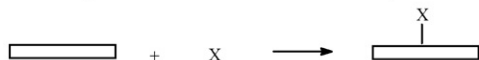
2. Trapping of adsorbed species X by Y:

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 $NB^{\cdot-}$ 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,
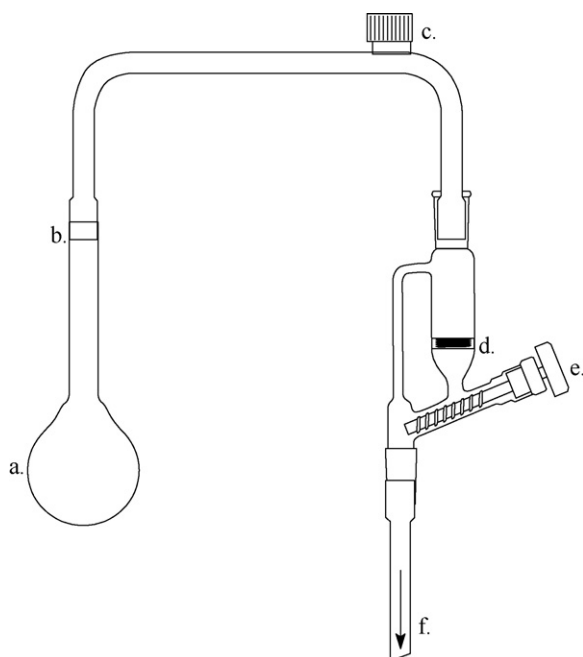
Fig. 1. Apparatus for chemical trapping studies (quartz bulb for catalysts' preparation (a), quartz-glass connection (b), septum (c), glass frit (d), Rotaflo stopcock (e), to high vacuum/dry argon system (f)).

HP-5 capillary column) in a total reaction time of 2 h using high purity octan-1-ol as an internal standard. The catalytic reactions were carried out several times for each catalyst under the same conditions. In each run, toluene conversion and C_8 selectivity were within the error range of ±2%.

2.5. Chemical trapping studies

The concentrations of the surface species identified by chemical trapping were not quantified due to the high relative error (very low concentrations). In this work the discussion will be based on qualitative analysis. All the adsorbates used in chemical trapping studies were fed in sequence.

2.5.1. Procedure for chemical trapping studies

Apparatus for chemical trapping is shown in Fig. 1. One gram of active catalyst (previously calcined at 900 °C for 3 h in the flow of dry air) was located in the quartz bulb (Fig. 1a) and degassed under 1.3×10^{-5} T at 900 °C for 3 h.

After cooling down to 750 °C (reaction's temperature), oxygen ($p = 2.7 \times 10^4$ Pa,), methane ($p = 1.3 \times 10^5$ Pa), oxygen and methane ($p = 2.7 \times 10^4$ Pa, $p = 1.3 \times 10^5$ Pa, respectively), oxygen and toluene ($p = 2.7 \times 10^4$ Pa and $p = 1.1 \times 10^3$ Pa, respectively) were added onto the catalyst and left in contact with the catalyst's surface for 1 h (all operations in dry conditions).

An excess of the appropriate trapping agent (see Table 2) was passed in through the septum (Fig. 1c).

After 20 min of contact with the trapping agent, the catalyst was cooled down to room temperature and then moved to the glass frit (Fig. 1d) and washed with a small amount of dry and deoxygenated benzene. The liquor was recovered by Rotaflo stopcock and analyzed by GC–MS (Hewlett Packard GC-6890/MSD-5973, HP-5 capillary column).

3. Results and discussion

3.1. Study of the strong monoelectron-donor properties (SMEDP)

The strong monoelectron-donor properties studied by EPR and their correlation with the catalysts' activity/productivity in the OMTM process are presented in Table 1. It is shown that the addition of either sodium or cesium ion onto the magnesium oxide surface increases approx. 22 times and 5 times, respectively the concentration of strong monoelectron-donor centers of the surface of magnesium oxide. Moreover, as it can be observed from Table 1, the synergetic effect of the simultaneous addition of two ions (1% Na$^+$ + 1% Cs$^+$) with a totally different atomic radii (0.97 and 1.67 Å for Na and Cs, respectively) increases tremendously (approx. 46 times) the concentration of centers with strong monoelectron-donor properties on the support (MgO). Confirmation of this behavior is found in the investigations of Kijenski et al. [24] and Khan and Ruckenstein [11] working on similar catalytic systems. Khan and Ruckenstein [11] found that the degree of covering by metals on the surface is higher if their atomic radii are different and that represents an increase in the basicity strength of the catalyst which made them more active in the OMTM process.

In terms of the specific activities in the OMTM process (mmol of toluene converted/m^2, Table 1), we observed higher activity (6.3 mmol T/m^2) of the catalytic system containing two ions than the catalysts with just one ion (for Na and Cs, 4.1 and 1.4 mmol T/m^2, respectively), and very low activity in the case of unmodified MgO (0.4 mmol T/m^2). As far as specific productivity is concerned, it is very clear that the catalyst containing two alkali ions is much more selective towards the production of C_8 fraction (1.2 mmol C_8/h m^2) than the other catalysts studied in this work (2.5-fold > 2%Na$^+$/MgO, 6-fold > 2%Cs$^+$/MgO and 12-fold > MgO, Table 1). The same synergetic effect in OMTM process was observed by Khan and Ruckenstein [11] using very similar catalytic systems. In this work, one very important observation to point out is: the higher the concentration of strong monoelectron-donor properties, the higher the activity/productivity in the OMTM process under our experimental conditions. The following activity-productivity-SMEDP decreasing sequence is observed: (1% Na$^+$ + 1% Cs$^+$)/MgO > 2% Na$^+$/MgO > 2% Cs$^+$/MgO > MgO. It is well known [24] that the strength of the electron-donor centers of magnesium oxide's surface modified by alkali metal ions is big enough to qualify it into the group of solid superbases. In our experimental conditions, this kind of superbasic centers were capable of activating toluene and methane in the presence of oxygen.

Table 1
Specific activity/productivity of the catalysts in oxidative methylation of toluene with methane in relation to the concentration of strong monoelectron-donor properties of the catalysts (HLSV = 52.2 mmol C_7H_8/($g_{cat.}$ h), toluene:methane:air = 1:12:12; reaction temperature, 750 °C, C_8 = EB + ST).

Catalyst	Specific activity, mmol of T converted/m^2	Specific productivity, mmol C_8/h m^2	Strong monoelectron-donor properties [a.u. NB$^{\rightharpoonup}$]/m^2
MgO	0.4	0.1	0.1
2% Na$^+$/MgO	4.1	0.5	2.2
2% Cs$^+$/MgO	1.4	0.2	0.5
1% Na$^+$ + 1% Cs$^+$/MgO	6.3	1.2	4.6

Table 2
Surface species of the reagents in the OMTM process identified by chemical trapping technique.
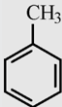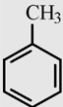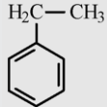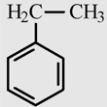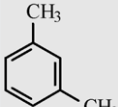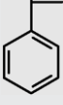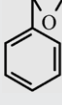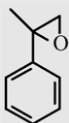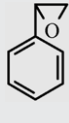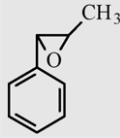
Entry	Catalyst	Adsorbate	Trapping agent	Products of trapping	Identified surface species
1	MgO	CH_4	[benzene]	None	None
2	MgO	CH_4	[cyclohexene]	None	None
3	$(1\%Na^+ + 1\%Cs^+)/MgO$	CH_4	[benzene]	None	None
4	$(1\%Na^+ + 1\%Cs^+)/MgO$	CH_4	[cyclohexane]	None	None
5	MgO	$O_2\ CH_4$	[cyclohexene]	None	None
6	MgO	$O_2\ CH_4$	[cyclohexane]	None	None
7	$(1\%\ Na^+ + 1\%\ Cs^+)/MgO$	$O_2\ CH_4$	[cyclohexene]	None	None
8	$(1\%\ Na^+ + 1\%\ Cs^+)/MgO$	$O_2\ CH_4$	[benzene]	[toluene: CH_3 on benzene]	$-CH_3$
9	$(1\%\ Na^+ + 1\%\ Cs^+)/MgO$	$O_2\ CH_4$	[toluene: CH_3 on benzene]	[ethylbenzene: H_2C-CH_3 on benzene]	$-CH_3$
10	$(1\%\ Na^+ + 1\%\ Cs^+)/MgO$	$O_2 CH_4$	[ethylbenzene: H_2C-CH_3 on benzene]	None	None
11	$(1\%\ Na^+ + 1\%\ Cs^+)/MgO$	$O_2\ CH_4$	[m-xylene: CH_3, CH_3 on benzene]	None	None
12	MgO	$O_2\ PhCH_3$	[benzene]	$PhCH_2C_6H_5$	$-CH_2Ph$
13	$(1\%\ Na^+ + 1\%\ Cs^+)/MgO$	$O_2\ PhCH_3$	[benzene]	$PhCH_2C_6H_5\ PhCH_2CH_2Ph$	$-CH_2Ph$
14	$(1\%\ Na^+ + 1\%\ Cs^+)/MgO$	$O_2\ PhCH_3$	[cyclohexene]	$PhCH_2C_6H_{11}\ PhCH_2CH_2Ph$	$-CH_2Ph$
15	MgO	O_2	[cyclohexane]	None	None
16	$(1\%\ Na^+ + 1\%\ Cs^+)/MgO$	O_2	[cyclohexene]	[cyclohexene oxide]	{O}
17	$(1\%\ Na^+ + 1\%\ Cs^+)/MgO$	O_2	[styrene]	[styrene oxide]	{O}

Table 2 (*Continued*)

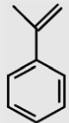| Entry	Catalyst	Adsorbate	Trapping agent	Products of trapping	Identified surface species
18	(1% Na$^+$ + 1% Cs$^+$)/MgO	O$_2$	(styrene)	(styrene oxide)	{O}
19	(1% Na$^+$ + 1% Cs$^+$)/MgO	O$_2$	H$_3$C–CH=CH$_2$	None	None
20	(1% Na$^+$ + 1% Cs$^+$)/MgO	O$_2$ CH$_4$	(styrene oxide)	(α-methylstyrene oxide) CH$_3$	CH$_3$
21	(1% Na$^+$ + 1% Cs$^+$)/MgO	O$_2$ CH$_4$	CH$_3$CH$_2$I	None	None
22	(1% Na$^+$ + 1% Cs$^+$)/MgO	O$_2$ CH$_4$	CO	None	None

3.2. Chemical trapping studies

Chemical trapping (according to the procedure explained in Section 2.5) is the method employed in this work to study the surface species formed after the adsorption of reagents on the catalyst's surface in the oxidative methylation of toluene with methane for two different catalysts in terms of activity/productivity/SMEDP (Table 2).

In the absence of oxygen and using benzene and cyclohexene as trapping agents, adsorbed surface species of methane were not detected in the presence of MgO and (1% Na$^+$ + 1% Cs$^+$)/MgO. Nevertheless, for (1% Na$^+$ + 1% Cs$^+$)/MgO, after oxygen pre-adsorption, methyl group was identified as a surface-specie. In this case, using benzene and toluene as trapping agents, toluene and ethylbenzene were obtained as trapping products, respectively (entries 8 and 9, Table 2). Methyl groups adsorbed on the oxidized surface of (1% Na$^+$ + 1% Cs$^+$)/MgO did not react with ethylbenzene and m-xylene (entries 10 and 11, Table 2) which is in very good agreement with our previous observations related to their low reactivity in the alkylation with methane [14].

In an effort to detect the methylene group (:CH$_2$) on the surface, as a potential product of oxygen and methane co-adsorption [25–27], cyclohexene was used as a trapping agent [19]; in this case, no trapping products were found (entries 6 and 7, Table 2).

On the surfaces of MgO and (1% Na$^+$ + 1% Cs$^+$)/MgO, after oxygen pre-adsorption and followed by adsorption of toluene, benzyl group (–CH$_2$Ph) was identified, nonetheless, in neither case benzylene group (:CHPh) was detected (entries 12–14 Table 2).

After changing the order of the reagents adsorption (firstly hydrocarbon and then oxygen), no trapping products were observed. This fact shows that the oxygen pre-adsorption is a "sine qua non" condition to make the OMTM process possible.

Very interesting results were obtained when (1% Na$^+$ + 1% Cs$^+$)/MgO (after oxygen adsorption under our reaction conditions) was left in contact with alkene molecules. Products of epoxydation were identified (epoxy-cyclohexene, styrene oxide and α-methylstyrene oxide) after reaction of alkenes (cyclohexene, styrene and α-methylstyrene) with the oxidized surface of (1% Na$^+$ + 1% Cs$^+$)/MgO (entries 16–18; Table 2). For this catalyst, propene did not furnish any product of epoxydation (entry 19, Table 2). Based on our results, we can claim that after adsorption of oxygen onto (1% Na$^+$ + 1% Cs$^+$)/MgO surface (unmodified MgO is not active), the oxygen molecule forms on the catalyst's surface some specific species, which are active in the epoxydation reaction, and certainly are responsible for the effective activation of methane (presently, we are carrying out experiments to identify those oxygen active species by EPR spectroscopy).

Methoxy group (–OCH$_3$) has not been detected on the surface of (1% Na$^+$ + 1% Cs$^+$)/MgO (entry 21, Table 2). To discover this group (–OCH$_3$), ethyl iodide was used as a trapping agent (formation of CH$_3$CH$_2$–OCH$_3$ after trapping) [19].

Carbon monoxide [19] was not an appropriate agent to trap adsorbed methyl group from the catalyst's surface (entry 22, Table 2).

3.3. Evidence of the proposed radical mechanism of OMTM process

The proposed radical mechanism for the oxidative methylation of toluene with methane (OMTM) by Otsuka et al. [13] has experimental evidence in this work. Chemical trapping was an easy and appropriate technique to confirm that hypothesis.

We can certify, in a very convincing way, that in our methylation conditions (>750 °C) the mechanism of OMTM is of radical type. Khan and Ruckenstein [11] proposed totally different conclusions for the same kind of catalysts as we are testing in this work. In their conclusions, catalytic surface centers responsible for the activation of reagents (abstraction of hydrogen in methane and hydrogen in the methyl group of toluene) in oxidative methylation of toluene are of ionic character (donor of two electrons) which are represented by O^{2-} surface sites, what means that the reaction is based on an ionic mechanism.

In our investigation, we determined by EPR spectroscopy that the highest concentration (4.6 [a.u. NB$^{\div}$]/m^2), among the tested catalysts, of the centers with strong monoelectro-donor properties was found on the surface of magnesium oxide modified with 1% Na and 1% Cs ions (see Section 3.1, Table 1). This catalyst showed the highest specific activity and productivity in the OMTM process. Only on the surface of this catalyst were methyl and benzyl groups identified by chemical trapping. Moreover, oxygen species were identified exclusively on the (1% Na$^+$ + 1% Cs$^+$)/MgO surface and they participated in the selective oxidation (epoxydation) of alkenes used as trapping agents. Obviously, we cannot declare with absolute certainty just based on the level of this research, which kind of oxygen species is responsible for methane and toluene activation (in our lab we are designing the suitable EPR spectroscopy experiments to detect all the paramagnetic species adsorbed on (1% Na$^+$ + 1% Cs$^+$)/MgO surface and detected by chemical trapping, including the identification of active oxygen species {O}).

Wang and Lunsford [28] identified O$^-$ species by EPR, which according to their conclusions are the sites responsible for the generation of methyl radicals in the oxidative coupling of methane to C$_{2+}$ under Li/MgO. We believe that the formation of O$^-$ anions is possible in our conditions by dissociation of oxygen (E_A = 0.46 eV [29]) thanks to the strong monoelectron-donor centers of the cata-

lyst (Eq. (3)). Lin et al. [30] proved that Eq. (3) could be the limiting step in oxidative coupling of methane under Na/CaO.

To sum up, we believe that the strong monoelectron-donor centers are the active sites responsible for the activation by dissociation of the molecular oxygen to O^- ion (reaction (1)) or O_3^- (resulting from the reaction of O^- and O_2 as it was proposed by Tench et al. [31,32], Naccache [33] and Wang and Lunsford [28] for the same kind of catalysts). It is shown in the literature [34], that O_3^- ions could be more responsible for the oxidation of $^\bullet CH_3$ radicals to CO_x than for the selective activation of methane.

In this work, the already formed oxygen species {O} (sine qua non-condition) are able to activate methane and toluene to get the respective radical species on the catalyst's surface (reactions (2) and (3)) which, following the Langmuir–Hinshelwood mechanism, form ethylbenzene (reaction (4)). In the last step of the reaction, ethylbenzene dehydrogenates to styrene whereas the active sites are regenerated (reaction (5)) closing the catalytic cycle. Based on our catalytic, EPR and chemical trapping studies, we believe that the radical mechanism of oxidative side-chain methylation of toluene with methane has now more convincing data for the scientific community, and it follows the bellow suggested steps:
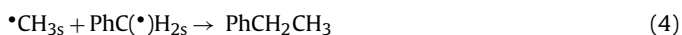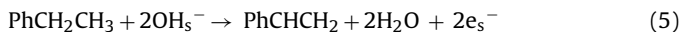
Adsorption and dissociation of oxygen

$$O_2 + 2e_s^- \rightarrow 2O_s^- \quad (1)$$

Methane and toluene adsorption onto the catalyst's surface

$$O_s^- + CH_4 \rightarrow {}^\bullet CH_{3s} + OH_s^- \quad (2)$$

$$O_s^- + PhCH_3 \rightarrow PhC(^\bullet)H_{2s} + OH_s^- \quad (3)$$
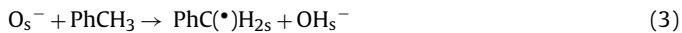
Surface coupling of methyl and benzyl radicals

$$^\bullet CH_{3s} + PhC(^\bullet)H_{2s} \rightarrow PhCH_2CH_3 \quad (4)$$

Dehydrogenation of ethylbenzene to styrene and strong monoelectron-donor centers' regeneration

$$PhCH_2CH_3 + 2OH_s^- \rightarrow PhCHCH_2 + 2H_2O + 2e_s^- \quad (5)$$

So far difficulties, related to the choice of a selective catalyst for the OMTM process and the tough task to optimize the process conditions, are due to the complexity of the process in which different reactions take place in a homo-heterogenized phase following a very complex mechanism of parallel and consecutive transformations.

It is worthy to point out that the chance of coupling of methyl and benzyl radicals in the gas phase is also high, as it happens in the oxidative coupling of methane to C_{2+} [35,36]. Osada et al. [37] tried to prove the mechanism of oxidative methylation of toluene with methane. In their studies, they used isotope-label toluene, $C_6D_5CD_3$, in the methylation reaction carried out at 700 °C in the presence of 3% Li_2O/Y_2O_3–CaO and under atmospheric pressure. They detected $C_6D_5CD_2CH_3$ as a product of coupling $^\bullet CH_3$ and $C_6D_5CD_2^\bullet$ radicals and claimed that the coupling occurred according to Langmuir–Hinshelwood mechanism as we observed in our studies and in the investigations of Otsuka et al. [13] as well.

Xu and Lunsford [38] showed the first spectroscopic prove of benzylic radicals for active catalysts in this type of reaction. Benzylic radicals were produced during the reaction of toluene with N_2O under Li/MgO and Sr/La_2O_3 at 650 °C, and the technique of Matrix Isolation Electron Spin Resonance (MIESR) was used for their detection [38].

We consider chemical trapping as a trustworthy and easy to apply method. The results coming from this work are providing the scientific community with one more convincing piece of evidence that the oxidative methylation of toluene with methane is governed mostly by a radical mechanism.

4. Conclusions

The findings generated in this study support the following conclusions:

1. It is shown that methane can be incorporated into the side chain of toluene in good C_8 specific yields (1.2 mmol $C_{EB+ST}/h\,m^2$) by the oxidative methylation in the presence of (1% $Na^+ + 1\%\ Cs^+$)/MgO at 750 °C under atmospheric pressure and toluene:air:CH_4 = 1:12:12 molar ratio.
2. Na + Cs incorporation onto the MgO surface enhances catalytic activity (1.5-fold, 4.5-fold and 16-fold more for Na/MgO, Cs/MgO and unmodified-MgO, respectively) and, what is much more important, alters positively the selectivity to C_8 fraction (ethylbenzene + styrene). 1 mol% Na + 1 mol% Cs/MgO is a better catalyst than MgO alone or modified with just one metal-cation for the reaction studied.
3. Modification of MgO surface by 1% Na and 1% Cs increases dramatically (synergetic effect of adding two different ions) the concentration (46 times higher than unmodified-MgO) of strong monoelectron-donor centers of the final catalyst.
4. Adsorbed benzyl groups were observed after the adsorption of oxygen and toluene on unmodified-MgO and (1% $Na^+ + 1\%$ Cs^+)/MgO, while adsorbed methyl group appears after the adsorption of oxygen and methane merely on the surface of (1% $Na^+ + 1\%\ Cs^+$)/MgO. Only on the surface of this catalyst, detected oxygen species are capable of the epoxydation of alkenes (cyclohexene, α-methylstyrene and styrene; negative proof for propylene). We believe that the strong monoelectron-donor centers of (1% $Na^+ + 1\%\ Cs^+$)/MgO take place in all performed adsorptions.
5. The experimental data coming out from chemical trapping and the strong monoelectron-donor properties of (1% $Na^+ + 1\%$ Cs^+)/MgO studied by electron paramagnetic resonance spectroscopy (EPR) are providing very important experimental evidence to confirm the existing hypothesis of the radical mechanism of the oxidative methylation of toluene with methane.

References

[1] R. Luque, L. Herrero-Davila, J.M. Campelo, J.H. Clark, J.M. Hidalgo, D. Luna, J.M. Marinas, A.A. Romero, Energy Environ. Sci. 1 (2008) 542.
[2] Kh.E. Khcheyan, O.M. Rovenko, A.V. Borisoglebskaya, D.L. Fishman, Zh. Org. Khim. 12 (1976) 467.
[3] Kh.E. Khcheyan, O.M. Rovenko, A.N. Shatalova, Proceedings of the 11th World Petroleum Congress, 4, 1983, p. 465.
[4] Kh.E. Khcheyan, O.M. Rovenko, A.V. Borisoglebskaya, Yu.Z. Kradkow, N.I. Yakovich, USSR Patent 639,844 (1978).
[5] N.I. Yakovich, L.P. Bokareva, A.G. Kostyuk, Pr-va Krupnotonnazh, Produktov Neftekhimii, Moskva, 1979, p. 37.
[6] K. Arishtirova, P. Kovacheva, N. Davidova, Appl. Catal. A 167 (1998) 271.
[7] L. Zhou, W. Li, M. Su, H. Li, K. Tao, H. Hattori, Appl. Catal. A 181 (1999) L1.
[8] P. Kovacheva, K. Arishtirova, S. Vassilev, Appl. Catal. A 210 (2001) 391.
[9] K. Arishtirova, P. Kovacheva, A. Predoeva, Appl. Catal. A 243 (2003) 191.
[10] K. Arishtirova, P. Kovacheva, A. Predoeva, React. Kinet. Catal. Lett. 84 (2005) 53.
[11] A.Z. Khan, E. Ruckenstein, J. Catal. 143 (1993) 1.
[12] E. Ruckenstein, A.Z. Khan, Appl. Catal. A 102 (1993) 233.
[13] K. Otsuka, M. Hatano, T. Amaya, J. Catal. 137 (1992) 487.
[14] J. Kijenski, P. Winiarek, J.C. Colmenares, Przem. Chem. 82 (2003) 721.

[15] Y. Osada, K. Enomoto, T. Fukushima, S. Ogasawara, T. Shikada, T. Ikaryia, J. Chem. Soc. Chem. Commun. 1156 (1989).
[16] T. Suzuki, K. Wada, Y. Watanabe, Ind. Eng. Chem. Res. 30 (1991) 1719.
[17] T. Suzuki, K. Wada, Y. Watanabe, Appl. Catal. 53 (1998) L19.
[18] A. Deluzarche, J. Hindermann, R. Kieffer, A. Muth, A. Papadopoulos, C. Tanielian, Tetrahedron Lett. 9 (1977) 797.
[19] A. Deluzarche, J. Hindermann, R. Kieffer, J. Mol. Catal. 31 (1985) 225.
[20] B.D. Flockhart, R.C. Pink, J. Catal. 4 (1965) 90.
[21] J. Kijeński, M. Marczewski, S. Malinowski, React. Kinet. Catal. Lett. 7 (1977) 151.
[22] O. Levenspeil, Chemical Reaction Engineering, John Wiley, New York, 1972.
[23] G. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, John Wiley, New York, 1990.
[24] S. Malinowski, J. Kijeński, in: C. Kemball, D.A. Dowden (Eds.), Catalysis, vol. 4, The Royal Society of Chemistry, London, 1980, p. 130.
[25] C. Lin, K.D. Campbell, J. Wang, J.H. Lunsford, J. Phys. Chem. 90 (1986) 534.
[26] G. Martin, C. Mirodatos, J. Chem. Soc. Chem. Commun. 1393 (1987).
[27] C. Mirodatos, G. Martin, in: M.J. Philips, M. Ternan (Eds.), Proc. 9th Int. Cong. Catal., vol. 2, Chem. Inst. of Canada, Calgary, 1988, p. 899.
[28] J.-X. Wang, J.H. Lunsford, J. Phys. Chem. 90 (1986) 5883.
[29] L.M. Branscomb, in: D.R. Bates (Ed.), Atomic and Molecular Processes, Academic Press, New York, 1962.
[30] C.H. Lin, J.-X. Wang, J.H. Lunsford, J. Catal. 111 (1988) 302.
[31] A.J. Tench, T. Lawson, J.F.J. Kibblewhite, J. Chem. Soc., Faraday Trans. I 68 (1972) 1169.
[32] A.J. Tench, J. Chem. Soc., Faraday Trans. I 68 (1972) 1181.
[33] C. Naccache, Chem. Phys. Lett. 11 (1971) 323.
[34] H. Yamamoto, H.Y. Chu, M. Xu, C. Shi, J.H. Lunsford, J. Catal. 142 (1993) 325.
[35] K.D. Campbell, E. Morales, J.H. Lunsford, J. Am. Chem. Soc. 109 (1987) 7900.
[36] K.D. Campbell, J.H. Lunsford, J. Phys. Chem. 92 (1988) 5792.
[37] Y. Osada, T. Fukushima, S. Ogasawara, T. Shikada, T. Ikaryia, J. Chem. Soc. Chem. Commun. 1434 (1990).
[38] M. Xu, J.H. Lunsford, J. Chem. Soc. Chem. Commun. 1203. (1995).