Catal Lett (2008) 121:199–208
DOI 10.1007/s10562-007-9347-7

Reductive Dehydration of Ethanol: A New Route Towards Alkanes

M. V. Tsodikov · F. A. Yandieva · V. Ya. Kugel · A. V. Chistyakov · A. E. Gekhman · I. I. Moiseev

Received: 31 July 2007 / Accepted: 6 November 2007 / Published online: 4 December 2007

Abstract New reactions, catalytic ethanol reductive dehydration into alkanes C_3–C_{10} and cross-coupling of ethanol with cyclopentanol into alkyl substituted cycloalkanes, were studied. The reductive dehydration of ethanol was carried out at 350 °C and 50 atm of Ar. The intermetallic hydrides with different hydrogen content, industrial Pt/γ-Al_2O_3 and reduced molten promoted iron catalysts were used as catalysts. The yield of alkanes varies depending on acid/base additives. The conversion of ethanol and the yield of higher alkanes increase as the hydrogen content in the intermetallic material decreases. When MgO is used as additive ethanol converts mainly into iso-alkanes. The content of iso-alkanes in the C_5–C_{10} fraction reaches 92%. The cross-coupling of ethanol with cyclopentanol over the catalytic compositions consisting of intermetallic hydride and Pt/γ-Al_2O_3 and reduced molten promoted iron afforded cyclic alkyl substituted hydrocarbons.

Keywords Ethanol reductive dehydration · Cross-coupling reaction · Alkanes · Oxygenates · Intermetallic hydride · Pt/γ-Al_2O_3 · Reduced molten promoted iron systems · Acid/base additives

Dedicated to Professor Sir John Meurig Thomas in the recognition of his pioneering contributions in catalysis.

M. V. Tsodikov (✉) · F. A. Yandieva ·
V. Ya. Kugel · A. V. Chistyakov
A.V. Topchiev Institute of Petrochemical Synthesis RAS,
Moscow, Russia
e-mail: tsodikov@ips.ac.ru

A. E. Gekhman · I. I. Moiseev
N.S. Kurnakov Institute of General and Inorganic
Chemistry RAS, Moscow, Russia

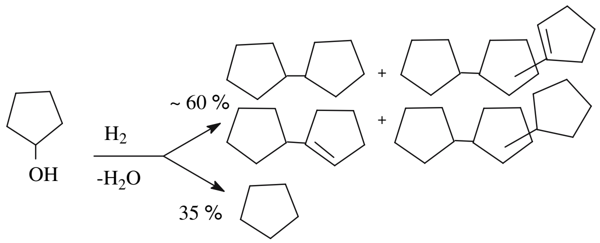
1 Introduction

Many catalytic transformations of alcohols have been known for more than a century [1]. Considerable study has been given to the redox reactions of alcohols catalyzed by metals and alloys [2, 3]. Reactions of alcohols catalyzed by both solid and liquid acids and bases have been studied intensively [3, 4].

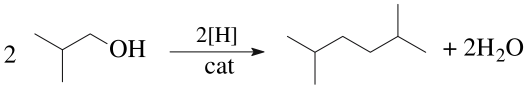
Chemistry of alcohols is of primary importance in the development and fundamentals of catalysis and in industrial applications [4–6]. Some fundamentals of catalytic science have been formulated based on studies of alcohol chemistry [1–11]. More than 70 millions tons of the bulk and fine chemicals are produced catalytically from C_1–C_4 aliphatic alcohols as feed stocks [1, 8].

Recently, a new catalytic reaction, alcohol reductive conversion into alkanes with at least doubled number of carbon atoms compared to the initial alcohol was reported [12, 13]. For instance, cyclopentanol was found to react with dihydrogen at 250 °C in the presence of an iron catalyst giving rise to a mixture of hydrocarbons containing cyclopentanyl and cyclopentanylidene fragments (see Scheme 1):

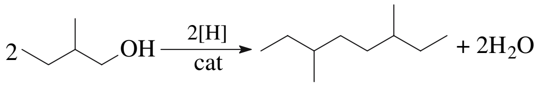
Analogously, benzyl alcohol or benzaldehyde (equilibrium between the alcohol and aldehyde is established under reaction conditions) reacts with H_2 in the presence of the reduced molten promoted iron catalyst (RMPIC) giving rise to 1,2-diphenylethane. Aliphatic alcohols, e.g., 3-methylbutanol and 2-methylpropanol, undergo a reductive conversion over the hydride $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ and Pt/Al_2O_3 catalyst yielding mainly alkanes with the doubled number of carbon atoms compared to the parent alcohol (see Eqs. 1 and 2) [13]:



Scheme 1 (dehydration of cyclopentanol) (250 °C, iron catalyst, $P_{H2} = 0.7$ MPa, H_2 flow rate $10^3\ h^{-1}$, alcohol feed rate $0.16 \div 0.18\ h^{-1}$)



(1)



(2)

A similarity between the reactions of alkanols, cycloalkanols and benzyl alcohol is clearly seen. The intermetallic hydride seems to be the major origin of the H atoms shown in brackets in Eqs. 1 and 2.

Based on the analogy with Eqs. 1 and 2, the reaction of ethanol in the presence of the hydride $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]\ H_{0.36}$ and Pt/Al_2O_3 catalyst was expected to produce *n*-butane as the main product (see Eq. 3):

$$2C_2H_5OH + 2[H] \rightarrow CH_3CH_2CH_2CH_3 + 2H_2O \qquad (3)$$

However, this reaction was found to be much more complicated than that shown in Eq. 3. In fact, the reaction products contained at most 0.1 wt.% *n*-butane, along with small amount of isobutane (see Eq. 4):

$$2C_2H_5OH + 2[H] \rightarrow (CH_3)_2CHCH_3 + 2H_2O \qquad (4)$$

Instead, the main reaction products were higher linear and branched alkanes that formed by ethanol reductive dehydration. Alkanes C_5–C_8 predominated in the alkane fraction [13]. In this paper the ethanol reaction is discussed in more detail.

2 Experimental

2.1 Catalytic Procedure

The reductive dehydration of ethanol and the combined transformation of cyclopentanol with ethanol were studied on a high-pressure flow-circulation setup with fixed-bed catalyst at 350 °C, 50 atm and alcohol VHSV 0.6 h^{-1}.

Ethanol and cyclopentanol, (analytical-grade) were used as received.

2.2 Catalysts

The intermetallic hydrides with different hydrogen contents, industrial $Pt/\gamma\text{-}Al_2O_3$ or reduced molten promoted iron were used as catalysts.

The intermetallic compound $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ was prepared by the consumed-electrode melting (2,400–2,600 °C) of the starting components. Titanium sponge (TG 100), low-carbon steel (Russian State Standard 11036-75), zirconium iodide and molybdenum metal were used as the starting materials. Prior to loading into the reactor, the intermetallic compound was crushed to 2–3 mm pellets using a ball mill with corundum balls. The intermetallic and $Pt/\gamma\text{-}Al_2O_3$ mixtures were prepared as thoroughly mixed blend consisting of 2–3-mm pellets of the intermetallic compound and small cylinders of the industrial $Pt/\gamma\text{-}Al_2O_3$ catalyst. The mixture of finely ground intermetallic compound (60 g) and $Pt/\gamma\text{-}Al_2O_3$ catalyst (7 g) was loaded in the reactor and the resulting heterogeneous system was treated with hydrogen at 100 °C and 1 atm under H_2 flow for 10–14 h (activation). After the activation, the system was cooled to 25–30 °C, and H_2 (100–120 atm) H_2 was fed in the circulation mode. Approximately 1 mol of H_2 was absorbed per the $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ unit, which amount corresponds to the $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_2$ hydride. Then $[TiFe_{0.95}Zr_{0.03}\text{-}Mo_{0.02}]H_2$ was partially dehydrogenated upon heating under Ar to the working temperature (350 °C), and the $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ hydride was formed. The subsequent oxidative treatments of $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ produced various hydride containing intermetallic species (See Table 1 samples I, III–VI).

MgO or $\gamma\text{-}Al_2O_3$ (analytical-grade) used as co-catalyst were introduced in an amount of 10% by weight based on the initial catalytic composition ($TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ + $Pt/\gamma\text{-}Al_2O_3$).

The reduced molten promoted iron catalyst was prepared by arc melting of natural magnetite with V_2O_5 promoter using water-cooled copper electrodes. The melting temperature of the oxide mixture was 1,500–1,600 °C, and the melting time was 60–120 s. The resulting alloy was crushed to a particle size of 2–3 mm and reduced with hydrogen at 450 °C and 0.1–5 MPa for 10–12 h.

2.3 Catalyst Pretreatment

Samples I and III–V were prepared by pretreatment of $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ with CO_2 (350 °C, 50 atm, 2 h);

Table 1 Activity of intermetallic hydride materials in ethanol to alkanes conversion (350 °C, 50 atm of Ar, $V_{ethanol} = 0.6\ h^{-1}$)

No.	Hydride composition	Alcohol conversion, % mol	Alkanes C_5–C_{10} yield on alcohol converted, % mol
I	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}$	33.5	–
II	Pt/Al_2O_3	66	0.4[a]
III	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18} + Pt/Al_2O_3$	64.2	4.5
IV	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02} + Pt/Al_2O_3 + MgO$	94	33.1
V	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1} + Pt/Al_2O_3 + \gamma\text{-}Al_2O_3$	72	5.5
VI	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_x + Pt/Al_2O_3$, where $x < 0.1$	96	20.3
VII	RMPIC	92	6.5

[a] Only *n*-olefins C_6–C_8 were detected

Sample VI was prepared by pretreatment of $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ with an Ar–air mixture ($[O_2] \sim 5\%$ vol) (350 °C, 50 atm, 2 h)

Sample VII was prepared by reduction of the Fe_3O_4/V_2O_5 alloy with H_2 (450 °C; 1 atm, H_2 flow rate 30 l/h)

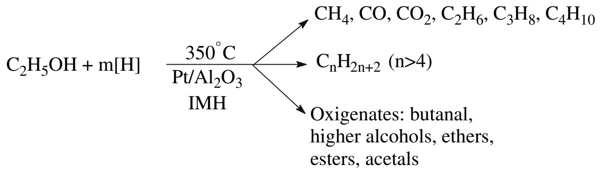
2.4 Product Analysis

The gaseous reaction products were analyzed by on-line gas chromatography using LKhM-80 and LKhM-8M chromatographs. The gas components were identified by reference compounds; their concentrations were calculated by the absolute calibration method. The H_2, CO, CH_4 and CO_2 samples were analyzed using analytical packed column *1* (5 m × 4 mm) with the SKT carbon sorbent (0.25–0.5 mm fraction), a heat-conductivity detector and special-purity grade Ar as the carrier gas. The C_1–C_4 hydrocarbons were analyzed on an analytical packed column (2 m × 4 mm) with $\alpha\text{-}Al_2O_3$ (0.25–0.50 mm fraction) modified with 2% squalane using a flame ionization detector.

The liquid products of alcohol conversion were analyzed on a Crystal-4,000 chromatograph (SE-30 phase) and a Kratos MS 25 RF chromatomass spectrometer using the packed and capillary columns.

3 Ethanol Conversion Over Intermetallic Hydride and Co-catalysts

In general, the reaction of ethanol yields a number of gaseous and liquid products (see Scheme 2):



Scheme 2 Main ways of ethanol conversion. IMH is intermetallic hydride

In the presence of the intermetallic hydride $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ and commercial $Pt/\gamma\text{-}Al_2O_3$ (10:1) catalyst composition ethanol is converted into gaseous and liquid alkanes and oxygen containing products (see Scheme 2 and Tables 1, 2, 3, 4). For instance, 64% of ethanol was converted giving rise to mostly C_1–C_4 alkanes and 4.5% mol C_5–C_{10} alkanes (see Experimental and Table 1, entry III) in the presence of the mixture of intermetallic hydride ($[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}$] and $Pt/\gamma\text{-}Al_2O_3$ catalyst at 50 atm of Ar and 350 °C.

Both the materials under study, the intermetallic hydride ($[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}$] and $Pt/\gamma\text{-}Al_2O_3$ catalyst, exhibited no catalytic activity in ethanol into alkanes transformation when used separately each other. Similarly, the yield of iso-C_{10} alkanes (listed in brackets below) from 3-methylbutanol reaction rose up in the succession: $[IMH + Al_2O_3]$ (0.6%) < Pt/Al_2O_3 (2.5%) < Al_2O_3 (4.9%) < $[IMH + Pt/Al_2O_3]$ (50%), suggesting a synergism of the IMH ≡ $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1}$ and Pt/Al_2O_3 activity [13].

Preliminary experiments showed the reaction is influenced by the catalysts mixture composition (including solid acid/base additives), hydrogen content in the intermetallic hydride and the method of IMH pretreatment.

4 Hydrogen Content in IMH

Our experiments showed that the reaction selectivity depends on both the composition of the intermetallic hydrogen carrier and hydrogen content. The data in Table 1 clearly show that both the alcohol conversion and higher alkanes yield tend to rise up as the hydrogen content in the intermetallic material decreases.

The intermetallic alloy TiFe is known [14] to absorb one mole of dihydrogen per TiFe unit forming the hydride $TiFeH_2$. Studies of H_2 thermodesorption [12] showed that the hydride $TiFeH_2$ splits off a dihydrogen molecule at room temperature. Our experiments demonstrated that ethanol converted into ethane mainly when contacting the

Table 2 Representative example of hydrocarbon products composition of ethanol conversion at 350 °C and 50 atm

No.	Systems	Yield of C2–C10 hydrocarbons, mmol				Yield of в C_2–C_{10} alkanes, mol %
		Alkanes			Alkenes	
		n-	i-	Total		
I	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}$	32	–	32	7	15[a]
II	Pt/Al_2O_3	36	0.4	36.4	503	7
III	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18} + Pt/Al_2O_3$	55.8	14.5	70.3	9.6	17
IV	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02} + Pt/Al_2O_3 + MgO$	113	154	267	6	53
V	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1} + Pt/Al_2O_3 + \gamma\text{-}Al_2O_3$	105	4	109	16	23
VI	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_y + Pt/Al_2O_3$, where $y < 0.1$	260	25	285	26	47
VII	RMPIC	104	6	120	45	40

[a] Alkenes and alkadiens C_2–C_4 were found in the presence of Pt/Al_2O_3

Table 3 Hydrocarbon gaseous products (350 °C, 50 atm)[a]

Catalysts	Gaseous products, mmol							
	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8	Total
$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}$ (**I**)	18.1	30.2	0.7	0.9	1.8	1.3	4.4	57.4
Pt/Al_2O_3 (**II**)	5.4	35.8	467.2	–	2.0	0.4	33.3	544.1
$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}/Pt/Al_2O_3$ (**III**)	18.7	32.7	0.3	1.4	0.1	3.1	1.4	57.7
$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}/Pt/Al_2O_3/MgO$ (**IV**)	27.8	84.3	–	3.2	0.2	13	1.2	129.7
$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1}/Pt/Al_2O_3/\gamma\text{-}Al_2O$ (**V**)	23.6	53.6	–	2.1	0.2	6.3	2.3	88.1
$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_y/Pt/Al_2O_3$, (**VI**) where $y < 0.10$	79.7	142.2	–	5	–	11.1	0.4	238.4
(VII) RMPIC	123	54	–	32	5	21	10	245

[a] A number of oxygenate products was formed under reaction condition besides alkanes (see scheme 2, Table 4)

intermetallic hydride $TiFeH_2$ under these conditions. The intermetallic hydride of composition $TiFe_{0.95}Zr_{0.03}Mo_{0.02}H_2$ was found to react analogously with ethanol at the temperatures below 350 °C.

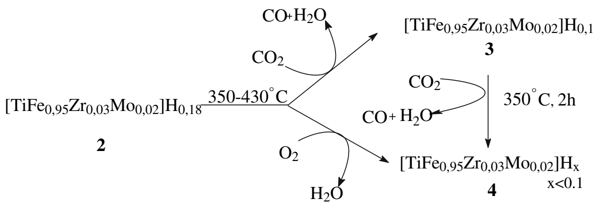
A number of hydrides based on the $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ alloy were tested as reducing agents in the reaction with ethanol. Earlier we found [15–17] that 1 mole of $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ absorbs 1 mole of H_2 to form the intermetallic hydride $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_2$. The thermal desorption curve of the adsorbed hydrogen from the sample of the stoichiometric composition $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_2$ in an argon atmosphere clearly exhibits three regions. The first of them corresponds to an intense release of 0.80–0.82 mol H_2 per mole of the sample in the range from 70 to 185 °C giving rise to the hydride of composition $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$, as shown by Eq. 5.

$$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_2 \xrightarrow{70-180\,^\circ C} 0.82H_2 + [TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36} \qquad (5)$$

The portion of dihydrogen evolved can be conventionally referred to as loosely bound hydrogen (LBH). Hydrogen contained in the intermetallic hydride $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ (**1**) is termed as strongly bound hydrogen (SBH). Hydride **1** is stable within the temperature interval 185–700 °C [15–17]. Part of SBH (~0.09 mol H_2 per mole of the intermetallic compound **1** was released from $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ within 700–920 °C (Eq. 6):

$$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36} \xrightarrow{700-920\,^\circ C} 0.09H_2 + [TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18} \qquad (6)$$

Much higher temperature is required for thermal desorption of the remaining hydrogen (~0.09 mol H_2 *per* IMH mol) from compound **2**. However, part of this SBH amount can be removed from the intermetallic hydride $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ by treatment with CO_2 or oxygen containing gas mixture at 350–430 °C (See Scheme 3) [9].



Scheme 3 Removal of hydrogen from metal hydride **2** by treatment of the hydride with CO_2 or dioxygen (6% of O_2 in Ar)

Table 4 Liquid oxygenates (350 °C, 50 atm of Ar)

Catalytic systems	Oxygenates (yield, mmol)				
	CO	CO_2	Alcohols	Aldehydes, ketones	Esters, ethers, acetals
$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}/Pt/Al_2O_3$ **(III)**	101.7	Traces	C_4H_9O-7.4 $C_6H_{13}OH$-0.3	–	$(C_2H_5)_2O$-160.2 C_2H_5-O-C_4H_9-4.3 C_2H_5-O-C_3H_7-2.2 $C_5H_{10}O_2$-30 $C_4H_7OOC_2H_5$-0.9
$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}/Pt/Al_2O_3/MgO$ **(IV)**	99.8	17.9	C_4H_9OH-8.2	C_2H_4O-4.3 C_4H_8O-3.3 $C_6H_{12}O$-2.8	$(C_2H_5)_2O$-37.2 C_2H_5-O-C_4H_9-8.2 $C_2H_4(OC_2H_5)_2$-1.5
$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1}/Pt/Al_2O_3/\gamma\text{-}Al_2O$ **(V)**	116.7	Traces	–	C_2H_4O-17.3 C_4H_8O-3.5	$(C_2H_5)2O$-161 C_2H_5-O-C_4H_9-27.8 $C_3H_6(OC_2H_5)_2$-6.6 $C_2H_5OC_7H_{15}$-0.7 $C_4H_8(OC_2H_5)_2$-0.8
$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_y/Pt/Al_2O_3$, where $y < 0.1$ **(VI)**	140	38.8	C_4H_9OH-2.2	C_2H_4O-3.9 C_4H_8O-1.7	$(C_2H_5)_2O$-16.4 C_2H_5-O-C_4H_9-7.7 $C_3H_6(OC_2H_5)_2$-2.6 $C_4H_7OOC_2H_5$-3.5 $C_2H_4(OC_2H_5)_2$-1.2
RMPIC **(VII)**	–	–	–	$C_5H_{10}O$-7.4 i$C_5H_{10}O$-1.7 $C_6H_{12}O$-5.0 $C_8H_{16}O$-0.9 $C_9H_{18}O$-0.4	–

CO_2 treatment of hydride **2** for a more extended time or repeated treatment of formed material, hydride **3,** (2 h at 350 °C) afforded a material containing less hydrogen amount, $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_x$, where $x < 0.1$. Analogously, hydrogen can be removed by careful oxidation of hydride **2** with the air–Ar mixture ($\sim$ 6% of O_2 vol.) as shown in Scheme 3 [16, 17].

The listed intermetallic hydrides in a combination with the $Pt/\gamma\text{-}Al_2O_3$ co-catalyst were tested in ethanol conversion (see Tables 1–3).

Intimate mixtures of the powdered intermetallic hydride materials **2–4** with the industrial $Pt/\gamma\text{-}Al_2O_3$ catalyst revealed catalytic activity in ethanol transformation to the higher alkanes, gaseous products and oxygenates. The results obtained (see Tables 1 and 2, entries III, IV and VI) show tend of rise the alkanes yield as hydrogen content in the intermetallic hydride is decreased.

5 The Role of Acid/Base Functions. MgO Promoting Effect

The acid groups and electronic vacancies capable of serving as acid centers and the basic groups (OH^-, H^-) could occur on the catalyst surface. Alcohols are known to undergo dehydration and condensation in the presence of solid acids like alumina [4, 5]. Hydrogenation catalysts (Cu, Pd, Rh, Ni, Cu/Cr, Ru-contacts) in combination with basic species are known to catalyze the Guerbet condensation of primary alcohols giving rise to branched higher alcohols, e.g. *iso*-butanol from propanol and methanol [7, 18–21]. Ethanol is known [21] to be converted into 1-butanol over the alkaline earth metal oxides and MgO modified catalyst at 450 °C.

Recently, in a study of CO_2 conversion with ethanol in the presence of the intermetallic hydride $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_2$ and the HIMC–γ–Al_2O_3–2% Pd/SiO_2 composition it was found [22] that the C_5–C_{14} alkanes were formed when the intermetallic hydride–alumina composition was preliminarily treated with carbon dioxide. In the presence of other compositions including intermetallic hydride combined with Pd/SiO_2, ethyl acetate was found as the main liquid product. The conversion of ethanol was determined in the presence of zeolite (ZSM-5) catalyst as support possessing Bronsted acidic sites [23]. Alkyl benzenes were the main products of ethanol conversion. Only negligible amount of light alkanes (up to C_5) was identified.

In this context, we examined the effect of alumina and magnesia additives to the catalytic composition under study.

Our experiments showed that the addition of γ-Al_2O_3 exerted no influence on the total alkane and *iso*-alkane yields (see Tables 1 and 2). The addition of 6 g of magnesia to the mixture of 6 g Pt/Al_2O_3 and 60 g $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ intermetallic hydride changed the properties of the system dramatically. After CO_2 treatment of the system (2 h at 350 °C), the hydrogen content in the hydride intermetallic was found to correspond to the composition $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}$ instead of $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}$ in the absence of MgO. Moreover, more than 28.3 mol% ethanol was converted into higher alkanes C_{5+} with the composition consisting of $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}/Pt/Al_2O_3/MgO$. This is much higher than that in the reaction of ethanol in the absence of MgO (entry IV).

The yield of *iso*-alkanes was found to enhance in the presence of MgO dramatically (see Fig. 1 and Table 2), while the hydrogen content in IMC in III-V systems initially corresponded to $[TiFe_{0.95}\ Zr_{0.03}\ Mo_{0.02}]H_{0.18}$. The reactivity of the compositions increased in the succession III < V <<< IV. As a consequence, hydrogen was exhausted from the V and IV systems faster than from the system III. As shown below, the hydrogen content in the IMH component affects the alkane distribution much less pronounced than it can be seen in Fig. 1. The extremal enhancement of iso-C6 yield should be attributed to the effect of magnesia additive.

Basic agents, e.g., $NaOCH_3$, are essentially important components of the Guerbet catalyst [9–11]. However, the Guerbet reaction is restricted by rather selective condensation of two alcohols molecules [7, 9–11]. For instance, the MgO-catalyzed condensation of two ethanol molecules (at 450 °C) was found as a way toward 1-butanol [21]. Hence, if the reaction in the presence of MgO would have been a version of the Guerbet reaction, an increase in the *n*-butanol yield should be expected. However, Fig. 2 shows that most part of alkanes formed in the presence of the Pt/γ-$Al_2O_3/[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}/MgO$ catalyst are $C_5 \div C_{10}$ alkanes. Moreover, the yield of *iso*-alkanes increased significantly in the presence of MgO containing system (Fig. 1).

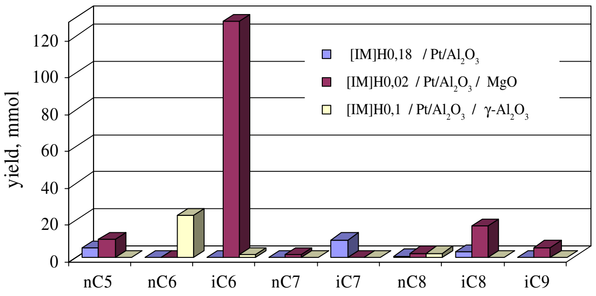


Fig. 1 Distribution of the alkanes C_5–C_{10} formed from ethanol in the presence of MgO containing $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}/Pt/Al_2O_3$, $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}/Pt/Al_2O_3/MgO$ and $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1}/Pt/Al_2O_3/\gamma$-$Al_2O_3$ systems. T—350 °C; P—50 atm. *X*-axis—Hydrocarbon fraction; *Y*-axis—Yield, mmol

The data available allow one to conclude that the acid centers are not involved into the reaction. In contrary to that, the basic centers seem to contribute into the higher alkane formation. However, the pathways of basic component participation in the reaction under study seem to differ from those in the Pt/γ-Al_2O_3 catalyst mediated reaction, which is used widely in alkane hydroisomerization.

The *iso*-alkanes formed from ethanol are not the products of normal hydrocarbons skeletal isomerization on platinum-alumina catalyst known to catalyse alkane isomerization.

The yield of C_6 fraction depends on the catalyst composition. However, the only component of mono-methyl substituted pentane fraction is 3-methylpentane, regardless of the catalyst used. 2-methylpentane expected as thermodynamically more stable reaction product was not found (see Scheme 4) [24–26]:

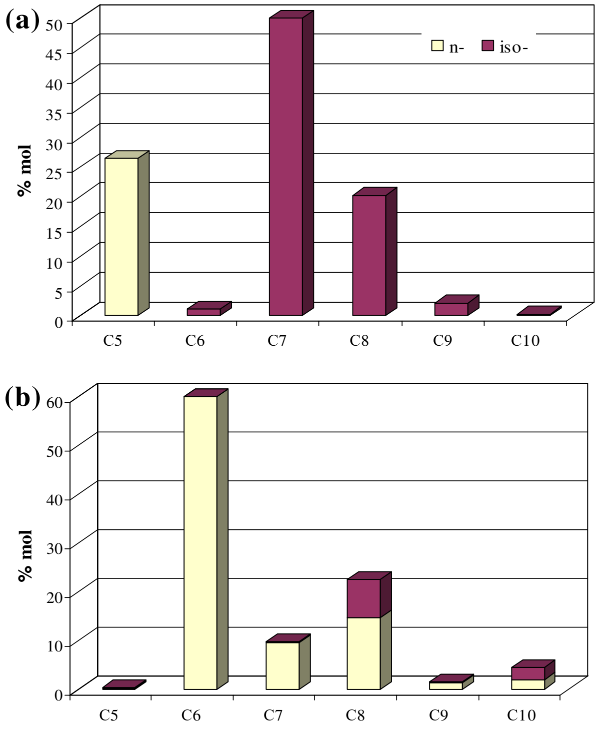
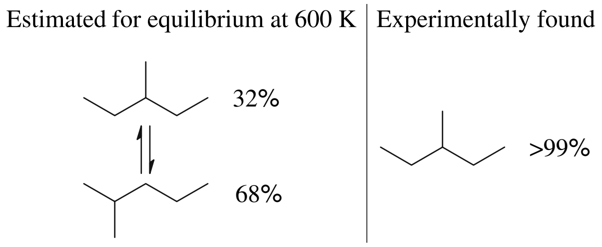


Fig. 2 The *n*- and *iso*-alkane distribution found with the catalyst $([TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}/Pt/Al_2O_3]$ (III) treated with CO_2 (**a**) and O_2 (**b**) (6% Air in Ar) (2 h, 350 °C). *X*-axis—Hydrocarbon fraction; *Y*-axis—Composition, mol%



Scheme 4 The ratio between 2- and 3-methyl-pentanes

These facts suggest the catalysts tested are not capable of performing the acid catalyzed skeleton isomerization of alkanes.

An important point is that the highest *iso*-alkane content was attained by adding basic magnesium oxide to the (IMC + Pt/γ-Al_2O_3) catalytic system. Note that the acid carrier γ-Al_2O_3 and the bifunctional catalyst Pt/γ-Al_2O_3, revealed no pronounced effect.

6 Role of Preliminary Catalyst Treatment

Alkane composition depends substantially on the mode of the preliminary treatment of the catalytic system resulting in removal of the intrinsically bound hydrogen. For instance, treatment of IMC with carbon dioxide (sample III) produced high amount of *iso*-alkanes, whereas the processing with a strong oxidizing agent like dioxygen provided preferential formation of *n*-alkanes (see Fig. 2).

7 Source of Hydrogen in the Reductive Dehydrogenation Reaction

It is clear that the amount of hydrogen contained in the intermetallic hydride is insufficient to cover the demand for the reaction observed. In fact, two H atoms are required to form ethane from an ethanol molecule (see Eq. 7):

$$C_2H_5OH + 2[H] \rightarrow C_2H_6 + H_2O \qquad (7)$$

Similarly, two H atoms are necessary to convert "n" molecules of ethanol into alkanes of composition $C_{2n}H_{2n+2}$ (see Eq. 8):

$$mC_2H_5OH + 2[H] \rightarrow C_nH_{2n+2} + mH_2O \qquad (8)$$

where $n = 2$ m

Taking into account Eqs. 7 and 8, one can estimate the hydride demand for alkane production in ethanol into alkanes conversion. The estimation point out that alkane formation requires much more hydrogen than it is available in the starting IMC hydride.

A major part of hydrogen is expected to come from side reactions responsible for CO, CO_2 and oxygenates formation. For instance, one mole of dihydrogen will be produced when one ethanol molecule eliminates carbon monoxide molecule:

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \qquad (9)$$

Water gas conversion of ethanol can be expected to give rise to two dihydrogen molecules per one molecule of carbon monoxide (see Eq. 10) [18].

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \qquad (10)$$

Analogously, formation of each mole of acetaldehyde and/or its derivatives (acetals) suggests the generation of one mole of dihydrogen per a mole of ethanol (see Eqs. 11, 12):

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \qquad (11)$$

$$2C_2H_5OH + C_2H_5OH \rightarrow CH_3CH(OEt)_2 + H_2O + H_2 \qquad (12)$$

The formation of an ester molecule will produce two dihydrogen molecules per two molecules of the ethanol reacted (see Eq. 13)

$$2C_2H_5OH \rightarrow CH_3CHOOC_2H_5 + 2H_2 \qquad (13)$$

The hydrogen content in catalytic system IV ($[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}$], (0.01 mole of H_2 per IMC unit) is quite insufficient to cover the demand for the observed conversion of ethanol into alkanes (see Table 1). Meanwhile, the contribution of the hydrogen eliminated from the ethanol consumed to form oxygenates according to Eqs. 9–13 satisfactory fills up this deficiency (see Table 5)

Approximately 0.2 moles of H_2 were required to form this amount of alkanes: 0.098 and 0.096 moles of hydrogen were consumed to form C_2–C_4 and C_5–C_{10} alkanes, respectively (see Eq. 8). The amount of hydrogen contained in the intermetallic hydride $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}$ (0.01 mol) is too small to convert ethanol into alkanes.

This observation is at variance with the assumption that the intermetallic hydride is a main reducing agent in the reaction under study. Moreover, the above analysis of reaction products suggests that the metal hydride in the III–VI systems contributes to only a small extent to alkane formation.

The data available suggest the reductive dehydration to be a dismutation reaction including two macro-kinetic steps:

- In the first step an ethanol molecule undergoes dehydrogenation (*e.g.*, *via* reactions Eqs. 9–13).

Table 5 Hydrogen evolution and consumption in ethanol reductive dehydration reaction (350 °C; 50 atm of Ar; IV [$TiFe_{0.95}Zr_{0.03}Mo_{0.02}$]$H_{0.02}$/Pt/$AI_2O_3$/MgO catalytic system)

Hydrocarbon	Found, mol	H_2 required, mol	Organic products of reactions (9)−(13)	Found, mol	H_2 emissed, mol
Ethane	0.09	0.084	Acetaldehyde	0.004	0.004
Propane	0.003	0.003	Butanal	0.003	0.002
i-Butane	0.001	0.001	1,1-diethoxyethane	0.002	0.001
Butane	0.013	0.012	Hexanal	0.003	0.002
Pentane	0.007	0.006	CO	0.100	0.100
i-Hexanes	0.08	0.077	CO_2	0.02	0.055
i-Heptanes	0.001	0.001	($TiFe_{0.95}$ $Zr_{0.03}Mo_{0.02}$)$H_{0.02}$	0.5	0.02
i-Octanes	0.008	0.010	dehydrogenation		
Octane	<0.001	<0.001			
$\sum$	0.203	0.194		–	0.180

- In the second step the hydrogen produced in the ethanol decomposition step is consumed to give rise to alkane molecules.

The hydrogen treatment of the starting intermetallic compound ($TiFe_{0.95}Zr_{0.03}Mo_{0.02}$) and the subsequent removal of the absorbed hydrogen seem to be the procedure necessary to create the active sites responsible for the conversion of ethanol into alkanes.

8 Reaction Catalyzed by Reduced Molten Iron Catalyst

Reduced molten iron promoted catalyst (RMPIC) was shown to exhibit activity in the reductive dehydration of ethanol at 350 °C. The yield of C_3–C_{10} alkanes reached 25 mol% (including 6.5% linear C_5–C_{10} alkanes) in the presence of RMIC catalyst (see Table 1 and Figs. 3, 4).

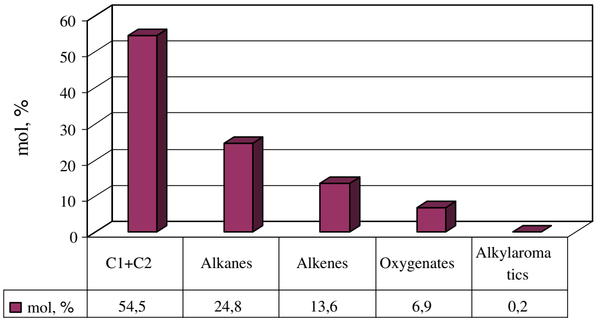


Fig. 3 The distribution of ethanol reductive dehydration products. (RMPIC, P—V_2O_5, 350 °C, 50 atm., EtOH feed rate = 0.6 h^{-1}). *X*-axis—Hydrocarbon type content; *Y*-axis—Composition, mol%

9 Cross-coupling of Alcohol Skeleton

Both ethanol and alicyclic alcohols have been shown to undergo reductive dehydration [12, 13, 16].

The reaction under study can be represented as an including oligomerization of fragments C_nH_{2n} supposedly formed upon splitting off an H_2O molecule from the alcohol. If the life-time of the hypothetical C_nH_{2n} species is high enough, the intermediates originated from different alkanols and different in structure and composition will gain a possibility to combine the formed alkanes with a carbon chain constructed from the residues of different alcohols. Keeping this in mind, we allowed a mixture of ethanol and cyclopentanol to react over the catalytic system discussed above.

In these experiments the yields of cyclic alkyl substitute hydrocarbons based on cyclopentanol passed, over [$TiFe_{0.95}Zr_{0.03}Mo_{0.02}$]$H_{0.1}$/Pt/ γ-Al_2O_3 and RMPIC systems were 6.4 and 10.1 mol%, respectively.

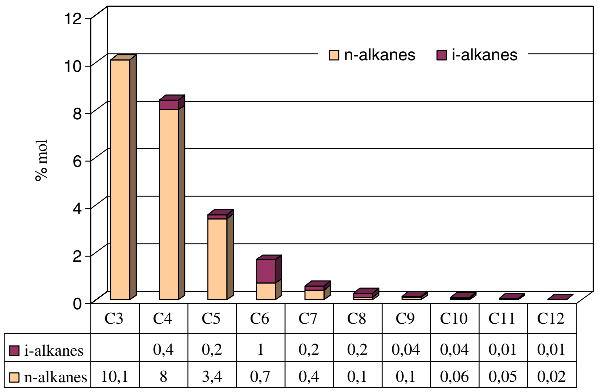
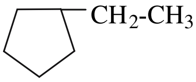
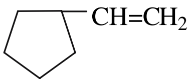
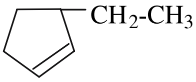
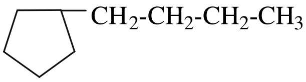
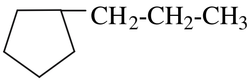
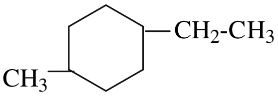
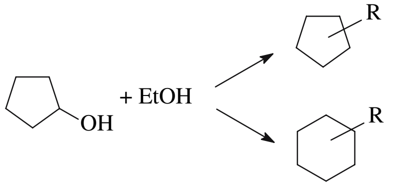


Fig. 4 The distribution of alkanes in C_3–C_{12} fraction (RMPIC, P—V_2O_5, 350 °C, 10 vol% of H_2 in Ar, V = 0.6 h^{-1}). *X*-axis—Hydrocarbon fractions; *Y*-axis—Composition, mol%

Table 6 Products of ethanol and cyclopentanol cross-condensation (50 atm.; 350 °C; alcohol feed rate 0.6 h^{-1})

Product names	Yield on cyclopentanol passed, % mol	
	$IMH_{0.1}$ + Pt/Al_2O_3 (after CO_2 treatment)	RMPIC
  	4.8	8.4
 	1.1	0.1
	0.6	1.6



where R (see Table 6) = C_2H_5; C_2H_3; C_3H_7; C_4H_9

Scheme 5 Cross-condensation of cylopentanol with ethanol (50 atm Ar, 350 °C, alcohol feed rate 0.6 h^{-1}; cylopentanol:ethanol = 1:1)

Table 6 presents the composition of alkyl substituted cyclic hydrocarbons, which could be attributed to ethanol and cylopentanol hydrocarbon skeleton cross-condensation products (Scheme 5):

The liquid fraction contains methylethylcyclohexane suggesting possible ring expansion of alkylcylopentane hydrocarbons that were found among the products besides alkyl substituted cyclopentanes. Table 7

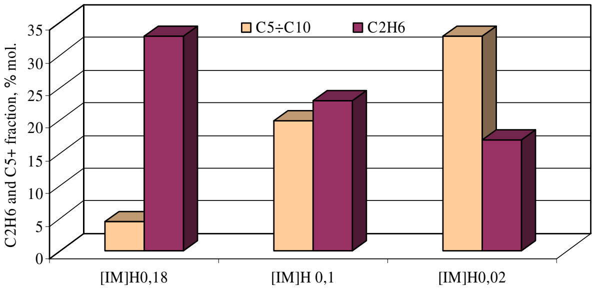


Fig. 5 Correlation between hydrogen content in the intermetallic system, ethane and alkane fraction C_{5+} yields (Catalysts: $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.18}/Pt/Al_2O_3$, III; $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1}/Pt/Al_2O_3$, V; $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}/Pt/Al_2O_3$, IV). *X*-axis—Intermetallic hydride composition; *Y*-axis—C_2H_6 and C_{5+} fraction, mol%

10 Conclusion

The catalytic systems under study do not vary in activities significantly. However, the ways of ethanol transformations seem to be different. Alkanes with even carbon atoms

Table 7 Catalytic systems used in experiments

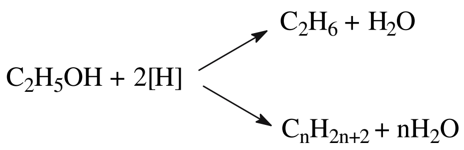
Sample no.	Catalyst content, g	Composition of prepared catalytic system
(I)	60	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1}$
(II)	7	Pt/Al_2O_3
(III)	60:7	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1}/Pt/Al_2O_3$
(IV)	60:7:7	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.02}/Pt/Al_2O_3/MgO$
(V)	60:7:7	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.1}/Pt/Al_2O_3/Al_2O_3$
(VI)	60:7	$[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_y/Pt/Al_2O_3$, where $y < 0.1$
VII	60	RMPIC

number are formed preferentially (up to 60–90%) depending on the reaction conditions with the intermetallic hydrides combined with the Pt/γ-Al_2O_3 catalyst (see Fig. 1). Contrary to that, alkanes with odd carbon atoms number formed preferentially in the presence of RMPIC (see Fig. 4).

Intermetallic compounds **2–4** contain strongly bound hydrogen (SBH). In experiments where those compounds were tested as the catalyst components this hydrogen should be taken in consideration while discussing the experimental data.

Figure 5 shows the relation between the yields of ethane and C_{5+} alkanes in the presence of catalytic compositions containing intermetallic hydride with different SBH content.

As clearly seen in Fig. 5, the smaller is the SBH content in intermetallic compound, the higher is the yield of alkane fraction and the lower is the yield of ethane. This result demonstrates the competitive nature of ethanol reduction into ethane and reductive dehydration reaction leading to the formation of high-molecular alkanes:



$$C_2H_5OH + 2[H] \rightarrow C_2H_6 + H_2O$$
$$C_2H_5OH + 2[H] \rightarrow C_nH_{2n+2} + nH_2O$$

The increased SBH content in the intermetallic hydride contributes to reaction (Eq. 6) domination and inhibition of condensation processes giving rise to high-molecular alkanes. In this context, the intermetallic compound can be considered as an agent transferring the hydrogen evolved in the course of the starting alcohol partial conversion to form hydrogen which is consumed in the alkane formation reaction (see Eqs. 1–4; 7–9).

Ethanol into *iso*-alkanes transformation was remarkably enhanced by the magnesia additives. In contrary to that, the reaction was not markedly affected by the addition of alumina. These data are in a contradiction with a mechanistic scheme assuming ethanol transformation *via* the known acid catalyzed reaction of alcohol or acetaldehyde like aldol condensation [4, 5]. However, the reaction under study resembles in some respects the Guerbet reaction providing iso-butanol from two ethanol molecules and in terms of aldol rationalized [7, 9–11]. Moreover, one could see that alkanes dominated in the reductive dehydration products in contrary to the Guerbet reaction wherein the alcohols with higher molecular mass prevailed.

The next step of reductive dehydration reactions evolution is cross-condensation of different alcohols skeleton, which was shown to proceed using cyclopentanol and ethanol as initial reagents.

Acknowledgment Financial supports by Russian Foundation for Basic Research (grant 05-03-32683), the Program of Presidium of the Russian Academy of Sciences No 7, and Federal Program for Scientific Schools Supporting (grant NS 4959.2006.3) are gratefully acknowledged.

References

1. Weissermel K, Arpe HJ (1993) Industrial organic chemistry. VCH, Weinheim
2. Rozovsky Aya, Lin GN (1990) Fundamentals of methanol synthesis process. Khimiya, Moscow (in Russian)
3. March J (1992) In: Advanced organic chemistry, reactions, mechanism and structure. J. Wiley and Sons, NY
4. Lebedev SV (1933) Zh Obsh Khimii 3:698 (in Russian)
5. Ostromislensky II (1915) Zhurn Russ Phys-Chem Obsh 47:1494
6. Vatsuro KV, Mishchenko GL (1976) Named reactions in organic chemistry. Chimiya, Moscow (in Russian)
7. Guerber M (1899) Compt Rend 128:511; 155 (1912) 1156
8. Astle MJ (1956) The chemistry of petrochemicals. Reinhold Publishing Corporation, NY
9. Carlini C, Girolamo MD, Marchionna M, Galleti AMR, Sbrana G (2002) J Molec Catal: A Chem 84:273
10. Carlini C, Girolamo MD, Maciani A, Marchionna M, Noviello M, Galleti AMR, Sbrana G (2003) J Molec Catal: A Chem 200:137
11. Cornils B, Herrmann WA, Schlogl R, Wong CH (eds) (2000) Catalysis from A to Z.A. concise encyclopedia. Wiley-VCH, Weinheim
12. Tsodikov MV, Kugel VV, Yandieva FA, Mordovin VP, Gekhman AE, Moiseev II (2004) Pure Appl Chem 76(9):1769
13. Moiseev II, Gekhman AE, Tsodikov MV et al (2004) In: Shibasaki, Yamamoto (eds) Catalysis by homo- and heteronuclear pollymetallic systems.. Wiley-VCH
14. Reilly JJ, Wiswall RH (1974) Inorg Chem 13:218
15. Tsodikov MV, Kugel VYa, Yandieva FA, Slivinskii EV, Moiseev II, Colon G, Hidalgo MC, Navio JA (2001) Stud Surf Sci Catal 138:239
16. Tsodikov MV, Kugel VYa, Yandieva FA, Kliger GA, Glebov LS, Mikaia AI, Zaikin VG, Slivinsky EV, Plate NA, Gekhman AE, Moiseev II (2004) Kinet Catal 45(6):854
17. Kochubey DI, Kriventsov VV, Maksimov YuV, Tsodikov MV, Yandieva FA, Mordovin VP, Navio JA, Moiseev II (2003) Kinet Catal 44(2):165
18. Ipatiev W (1908) Katalytische reactionen bei hohen Temperaturen und Druchen. XIV. Hydrogenisation des Benzylaldehydes und des Benzylalkohols in Gegenwart von Eisen, Ber. 41:993
19. Thomas ChL (1970) Catalytic processes and proven catalysts. Tempe. Arizona, Academic Press, New York and London
20. Ponec V, Bond GC (1995) Catalysis by metals and alloys. Elsevier, Amsterdam
21. Ndou AS, Plint N, Coville NJ (2003) J Appl Catalys A 251:337
22. Tsodikov MV, Kugel VYa, Slivinskii EV et al (1999) Langmuir V15:6601–6604
23. Tretyakov VPf (2006) Catal Indust V4:11–17
24. Olah G, Tolgyesi W, Kuhn S, Moffat M, Bastien J, Baker E (1963) J Am Chem Soc 85:1328
25. Olah GA, Molnar A (1995) Hydrocarbon chemistry. John Wiley and Sons, Inc., New York, Chichester, Brisbane, Toronto, Singapore
26. Stull DR, Westrum EF, Sinke CG (1969) The chemical thermodinamics of organic compounds. Wiley, NY