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Activity of vanadium magnesium oxide supported catalysts in the dehydrogenation of isobutane

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The activity of the vanadium magnesium binary oxides supported on C_{act}, SiO_2, γ-Al_2O_3 and ZnO in the dehydrogenation of isobutane to isobutene under the carbon dioxide or inert gas atmosphere was investigated. The highest isobutene yield (34.8%) was obtained over active carbon supported catalyst. The role of carbon dioxide in the dehydrogenation process was determined on the basis of additional tests: the RWGS reaction, gasification of coke and regeneration of partially reduced catalysts. The temperature-programmed techniques (TPR-H_2, TPD-NH_3 and TPD-CO_2) were used to characterize the catalysts.

KEY WORDS: isobutane dehydrogenation; $VMgO_x$ supported catalysts; role of carbon dioxide.

1. Introduction

At present, isobutene is typically obtained by catalytic dehydrogenation of isobutane and as a by-product of steam cracking or a fluidized catalytic cracking of naphtha. The AAB Lummus Global, the world leader of catalytic dehydrogenation technology, have licensed eight CATOFIN® process units, which provide isobutylene with an aggregate capacity of about 2.8 million metric tons per annum (MTA) [1,2]. Dehydrogenation of isobutane is known as an equilibrium and endothermic reaction (1).

$$
\begin{gathered}
iC_4H_{10} \rightleftharpoons iC_4H_8 + H_2 \\
\Delta H^o_{298} = 117.28\,\mathrm{kJ/mol}
\end{gathered}
\tag{1}
$$

For thermodynamics reasons, significant yield of alkene requires operation at relatively high temperatures what causes high-energy costs. Moreover, such process conditions favor undesired thermal cracking reactions to lighter hydrocarbons and leads to rapid catalyst deactivation by coke [3–5].

An alternative to this process is an oxidative dehydrogenation (ODH) of isobutane by molecular oxygen (2).

$$
\begin{gathered}
iC_4H_{10} + 0.5O_2 \rightarrow iC_4H_8 + H_2O \\
\Delta H^o_{298} = -124.68\,\mathrm{kJ/mol}
\end{gathered}
\tag{2}
$$

The ODH gives the following benefits: the reaction is irreversible and exothermic, process can be carried out at lower temperatures and there is no carbon deposition deactivating the catalyst. However, using oxygen as an oxidant of isobutane brings several problems, such as flammability of the reaction mixture, necessity of the heat removal and the presence of deep oxidation reactions, which are very hard to control. These side reactions lower the process selectivity due to the production of undesired carbon oxides [4–6]. Therefore, it is expected that replacing oxygen in the oxidative dehydrogenation reactions by weak oxidants, such as SO_2, N_2O and CO_2, will suppress these disadvantages [7–10].

Recently, several attempts were made to use carbon dioxide as an unconventional source of oxygen in the oxidative dehydrogenation of isobutane [9–16]. The overall reaction can be described as follow (3):

$$
\begin{gathered}
iC_4H_{10} + CO_2 \rightleftharpoons iC_4H_8 + CO + H_2O \\
\Delta H^o_{298} = 158.41\,\mathrm{kJ/mol}
\end{gathered}
\tag{3}
$$

It has to be pointed out that the dehydrogenation of isobutane in the presence of carbon dioxide can proceed by two different reaction pathways. The first one is a direct process, shown in the equation 3, where the CO_2 promotes the dehydrogenation through reoxidizing the catalyst surface, reduced by isobutane. This one-step pathway is in agreement with the Mars and van Krevelen mechanism [11,12]. The second one, known as a two-step pathway, is a simple dehydrogenation (equation 1) followed by the reverse water gas shift reaction (RWGS, equation 4):

$$
H_2 + CO_2 \rightleftharpoons H_2 + CO \qquad \Delta H^o_{298} = 41.13\,\mathrm{kJ/mol} \tag{4}
$$

In this case CO_2 removes hydrogen from the reaction system and releases the thermodynamic limitation of equilibrium [4]. Many results indicate that isobutene is formed by both presented mechanisms [11,12]. Moreover, in the dehydrogenation process carbon dioxide can

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act as a diluent, it delivers the required heat and reduces coking of catalyst by the coke gasification [10–15]:

$$C_{coke} + CO_2 \rightleftharpoons 2CO \qquad \Delta H^{o}_{298} = 172.42\,\mathrm{kJ/mol} \quad (5)$$

In our previous papers we presented the results of isobutane dehydrogenation with carbon dioxide over vanadium magnesium oxides [16,17] and vanadium oxide catalysts loaded on different supports [18]. We found that $VMgO_x$ catalyst (V/Mg = 0.11 molar ratio) prepared by citrate method exhibit relatively high activity in the dehydrogenation of isobutane. The presence of carbon dioxide enhanced the alkane conversion [17], as in the case of the active carbon supported vanadium oxide [18]. The opposite trend was observed over VO_x/Al_2O_3 and VO_x/ZnO catalysts while silica supported vanadium oxide didn't show considerable sensitivity to the reaction atmosphere [18]. Those experiments brought us the question how much the catalytic performance and the physicochemical properties of the vanadium magnesium oxide catalyst can be changed by loading it on the new mentioned supports. To find the answer, catalytic tests with isobutane and carbon dioxide were carried out together with the temperature-programmed reduction and desorption analysis.

2. Experimental

The supported $VMgO_x$ catalysts with the V/Mg molar ratio of 0.11 were prepared by combined impregnation - citrate method. The supports: C_{act}, γ-Al_2O_3, SiO_2 and ZnO were suspended in a transparent aqueous solution of ammonium metavanadate, magnesium nitrate and citric acid in such amount to yield a nominal 4 wt% of V_2O_5. Next, the slurry was evaporated at 353 K while stirring, and then dried at 373 K for 12 h. Except the active carbon supported catalyst, the solid precursors were calcined in static air at 923 K for 6 h, pressed to thin discs and crushed to form the final bulk catalyst samples (d = 0.2–0.3 mm). Prior the impregnation the silica gel was dried for 3 h at 180 °C to obtain anhydrous silicon dioxide. All the supports were powdered while the activated carbon was crushed to the particles with 0.2–0.3 mm diameter. The unsupported $VMgO_x$ catalyst was prepared by the citrate method [17].

The dehydrogenation of isobutane to isobutene was carried out under atmospheric pressure at 873 K. Prior to the reaction, the catalysts were placed in a reactor and outgassed in helium for 0.5 h. Then the reactor was fed with iC_4H_{10} and CO_2 (or He) in the molar ratio of 1:6 and total flow rate 35 $cm^3\ min^{-1}$. In the case of active carbon supported catalyst, the sample was first activated at 923 K in carbon dioxide flow (30 $cm^3\ min^{-1}$). After 10 min, the temperature was lowered to 873 K and the sample was degassed for further 10 min in helium. The products formed during the dehydrogenation were analyzed on-line with two gas chromatographs. The details were given elsewhere [16,17].

The specific surface area (BET method) of the catalysts was determined at 77 K using nitrogen as the adsorbate. The temperature-programmed studies were carried out in a quartz reactor connected on-line with a thermal conductivity detector. All the samples were pretreated using the same procedure as that used for the catalytic tests. For TPD-NH_3 and TPD-CO_2 experiments, the outgassed samples (0.2 g) were cooled to room temperature under dry helium flow and than saturated with ammonia or carbon dioxide for 0.5 h (30 $cm^3\ min^{-1}$). The unadsorbed gases were flushed out of the reactor by flowing helium (60 $cm^3\ min^{-1}$), and finally the temperature was increased to 873 K at the heating rate of 10 K min^{-1}. Desorbed species were analyzed on-line. For the TPR-H_2 experiments the catalysts were taken in such amounts as to give the samples with 8 mg of V_2O_5 content. The catalysts were reduced with the mixture of hydrogen and argon (1:9 volume ratio, 30 $cm^3\ min^{-1}$) by programming the temperature from room temperature to 900 K at the constant heating rate of 10 K min^{-1}. The maximum temperature was kept unchanged, until the rate of hydrogen consumption returned to the initial value. The TCD peak areas were calibrated by injections of dry, gaseous ammonia, carbon dioxide and pure argon for TPD and TPR experiments respectively. The reduction extent of V species $(H_2/V)_{mol}$ and the average formal oxidation number of vanadium after TPR-H_2 analysis were calculated [19].

3. Results and discussion

Figure 1 shows the isobutane conversion and isobutene selectivity as a function of the reaction time at 873 K. The process was carried out both in the presence and absence of carbon dioxide. To minimize the adverse thermal effect and to keep the vanadium content in the samples at the same level of 18 mg V_2O_5, precisely 0.4 g of the supported catalysts were taken to the catalytic tests. Moreover, the unsupported $VMgO_x$ was diluted with glass grains (weight ratio of 1:4) what allowed obtaining the reactor packing with the same vanadium content. To identify the possibility of thermal dehydrogenation of isobutane over the glass, blank test also has been carried out (0.4 g of glass particles with 0.2–0.3 mm diameter).

For unsupported vanadium magnesium oxide and active carbon supported catalyst after 10 min of the reaction, the isobutane conversion was higher in the presence of carbon dioxide than that under helium atmosphere. However, when the reaction period was increased, the reduction of catalyst activity was lower in the presence of helium. Therefore, the isobutene yield in the CO_2 was higher only at the first part of process. Only

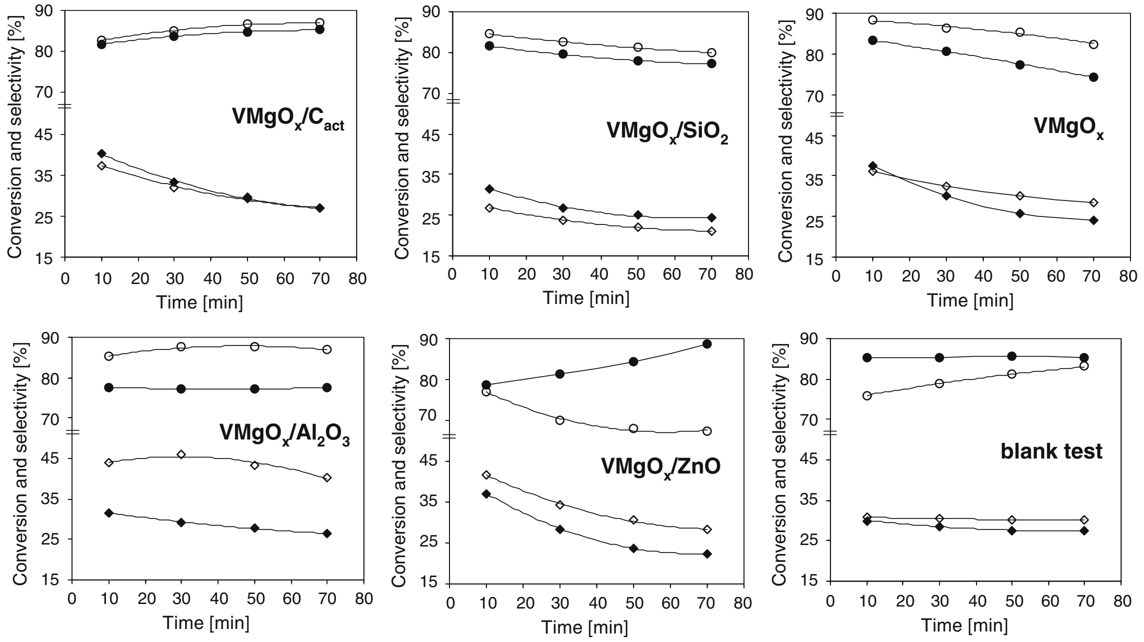

Figure 1. The isobutane conversion (◆) and isobutene selectivity (●) as a function of the reaction time at 873 K in the presence (solid symbols) and absence (open symbols) of CO_2.

in the case of silica supported vanadium magnesium oxide, the isobutane conversion in the carbon dioxide flow was higher than that in helium during the whole experiment. The opposite trend was observed when the dehydrogenation was carried out over $VMgO_x/Al_2O_3$ and $VMgO_x/ZnO$ – then the isobutene yield in helium was higher than that in the presence of carbon dioxide. Moreover, the catalytic activity of the alumina supported vanadium magnesium oxide gradually increased to a small extent during the first 30 min of the run in helium atmosphere. Thermal dehydrogenation over glass particles gave traces of isobutene (~1% yield) in the both atmospheres.

Because of the rapid catalyst deactivation, the most interesting are first minutes of the dehydrogenation process. Data presented in table 1 show initial average results of the isobutane dehydrogenation over the vanadium magnesium oxide catalysts used in this work. To measure the average conversion and selectivity within first 10 min of the process, the gases at the reactor outlet were collected in separate bottles and then analyzed chromatographically.

Table 1
The average values of the conversion and selectivity for the catalytic dehydrogenation of isobutane* over unsupported $VMgO_x$ and supported vanadium magnesium oxide catalysts

Catalyst	Feed composition	Conversion (%)		Molar ratio		Selectivity (%)				
		iC_4H_{10}	CO_2	CO/iC_4H_8	H_2/iC_4H_8	iC_4H_8	$C_3H_8 + C_3H_6$	$C_2H_6 + C_2H_4$	CH_4	*n*-butenes
Blank test	iC_4H_{10}/He	2.1	–	0.0	0.7	60.4	32.0	0.6	6.9	–
	iC_4H_{10}/CO_2	2.7	0.2	0.5	0.0	77.2	18.8	0.2	3.8	–
$VMgO_x$	iC_4H_{10}/He	6.6	–	0.2	1.4	78.8	16.4	0.3	4.5	–
	iC_4H_{10}/CO_2	7.2	3.6	3.2	0.2	73.5	1.6	0.5	4.4	–
$VMgO_x/C_{act}$	iC_4H_{10}/He	42.0	–	0.1	2.0	77.7	12.0	1.0	9.3	0.1
	iC_4H_{10}/CO_2	45.5	7.2	2.1	1.6	76.4	12.6	1.1	9.8	0.1
$VMgO_x/SiO_2$	iC_4H_{10}/He	5.5	–	< 0.1	0.7	85.5	11.7	0.2	2.3	0.2
	iC_4H_{10}/CO_2	6.6	1.3	1.1	0.4	81.5	14.3	0.3	3.5	0.4
$VMgO_x/Al_2O_3$	iC_4H_{10}/He	24.4	–	0.2	1.7	82.8	10.9	1.2	3.9	1.1
	iC_4H_{10}/CO_2	16.4	11.4	4.5	0.6	76.9	14.4	1.9	6.0	0.7
$VMgO_x/ZnO$	iC_4H_{10}/He	8.9	–	0.4	1.2	54.0	34.0	2.0	9.9	–
	iC_4H_{10}/CO_2	7.4	4.3	4.6	0.3	52.6	33.0	4.8	9.2	0.4

*Reaction conditions: 873 K, $iC_4H_8/CO_2(He) = 1/6$ (molar ratio), total flow rate = 35 $cm^3\ min^{-1}$, 18 mg V_2O_5 in 0.4 g reactor package, analysis of products collected within first 10 min of the process.

The main products of the isobutane dehydrogenation were isobutene, propene and methane. There were also small amounts of propane, ethane and ethylene. Only over alumina, silica and active carbon supported catalysts traces of n-butenes were detected in the both reaction atmospheres. The selectivity to n-C_4 hydrocarbons was constant during the isobutane dehydrogenation, except for the $VMgO_x/C_{act}$ catalyst, where *n*-butenes disappeared after 0.5 h of reaction. The presence of the isomerization products can be explained by relatively strong acidity of the catalysts (table 2). This effect is related to the fact that isobutane and larger hydrocarbons have a negative charge on the most reactive hydrogen, what favors their interaction with electrophilic (acidic) surfaces. Nevertheless, electron-donating olefins are more basic than the corresponding paraffins, so their desorption from acidic surfaces is more difficult [20,21]. Strong interaction with the catalyst surface may promote further isomerization and degradation of the dehydrogenation products to coke, which was confirmed by our experiments. Except for hydrocarbons, hydrogen, carbon oxide and water were detected. Small amount of CO detected during the isobutane dehydrogenation in helium could come from interaction of lattice oxygen with the reagents. Formation of atomic oxygen from magnesium orthovanadate ($Mg_3V_2O_8$), proposed by Burrows *et al.* [22], proceeds according to the equation (6) with simultaneous reduction of vanadium ions from V^{+5} to V^{+3}

$$Mg_3V_2O_8 \rightarrow 2MgO + MgV_2O_4 + 2O \qquad (6)$$

The subsequent reaction of atomic oxygen with H_2 shifts the dehydrogenation equilibrium. This can explain the small growth of the isobutane conversion, which was observed over alumina supported catalyst during the first 30 min of the process carried out in helium atmosphere. For the same reason and the possibility of further hydrogenolysis, the H_2/iC_4H_8 molar ratio was below one for the dehydrogenation of isobutane in helium over $VMgO_x/SiO_2$ catalyst.

Table 2

The average CO yields for the reaction of CO_2 with hydrogen (RWGS), coke (gasification) and reduced vanadium (reoxidation) in comparison with the blank test (fresh catalyst)*

Catalyst	The average yield of CO (%) from			
	Blank test	Gasification	RWGS	Reoxidation
$VMgO_x$	–	Traces	1.0	Traces
$VMgO_x/C_{act}$	0.4	0.4	4.0	0.8
$VMgO_x/SiO_2$	Traces	< 0.1	0.9	< 0.1
$VMgO_x/Al_2O_3$	Traces	0.5	9.8	0.3
$VMgO_x$/ZnO	–	0.3	11.7	0.4

*Reaction conditions: 873 K, CO_2 flow rate = 30 cm^3 min^{-1}, 18 mg V_2O_5 in 0.4 g reactor package, analysis of products collected within first 10 min of the each process. The yield below 0.01% denoted as traces.

In the presence of an oxidizing agent (CO_2) the lattice oxygen becomes available for the Mars and van Krevelen reaction mechanism [11,12], but it is known from the literature that the reversibility of the reaction (6) is very low [22]. Therefore, most of carbon oxide produced during the dehydrogenation in CO_2 atmosphere comes from the reverse water gas shift reaction (4) and the gasification of coke (5). To confirm this hypothesis additional tests were carried out.

A stream of CO_2 (30 cm^3 min^{-1}) was passed through the fresh, coked and partially reduced catalyst at 873 K. All the products were collected during the first 10 min of each test and analyzed chromatographically. Carbon oxide yields calculated from the tests (i.e., the blank test, the gasification of coke and the reoxidation of vanadium respectively), were compared with the average amount of CO formed in the RWGS reaction (H_2:CO_2 = 1:6 molar ratio). From the data presented in table 2 it is clearly seen that the highest CO yields were obtained during the reverse water gas shift reaction. The blank tests over unsupported $VMgO_x$ and supported alumina, silica and zinc oxide catalysts, showed that carbon dioxide does not interact with the vanadium at high oxidation state. Although considerable amount of CO was formed over freshly activated $VMgO_x/C_{act}$, we have to take into account the nature of the support, which can interact with the carbon dioxide in the Boudouard reaction (5). Moreover, the TPR-H_2 and XRD analysis proved that active carbon supported catalysts contain vanadium oxide at a lower oxidation state [18,23]. Therefore, the carbon dioxide can also participate in reoxidation of the catalyst. Possibility of such reaction was confirmed by the tests with partially reduced catalysts, where measurable amounts of CO were detected.

The nature of the catalyst surface was tested by temperature-programmed desorption of NH_3 and CO_2. As the probe gases were adsorbed at room temperature, the first peak (up to 373 K) should be associated with the physisorbed NH_3 and CO_2. The higher temperatures maxima can be assigned to desorption of chemisorbed species from the sites of different strength [24]: weak (below 473 K), medium (473–573 K) and strong (above 573 K). The amounts of desorbed ammonia and carbon dioxide were calculated from the overall TCD signal areas, calibrated by injections of pure NH_3 and CO_2. The percentage of strong acidic (basic) site were determined from the ratio of the TPD area for the particular temperature region, to the TPD area associated with chemisorption (table 3).

The percentage of strong basic sites in $VMgO_x$ supported catalysts decreases in the sequence: ZnO > Al_2O_3 > C_{act} > $VMgO_x$ > SiO_2. The same order is observed for the average carbon oxide yields in the reverse water gas shift reaction (table 2). Moreover, the CO/iC_4H_8 molar ratios obtained for the dehydrogenation in carbon dioxide flow (table 1) decrease in similar

Table 3
The catalysts BET surface areas and the results from TPD experiments

Catalyst	BET (m^2/g)	NH_3 desorption (mmol NH_3 /g_{cat})			CO_2 desorption (mmol CO_2/g_{cat})			Overall NH_3/CO_2
		Total	> 373 K	Strong acidic sites* (%)	Total	> 373 K	Strong basic sites* (%)	
$VMgO_x$	20.9	0.71	0.41	15	0.29	0.18	18	2.5
$VMgO_x/C_{act}$	359.3	1.87	1.20	17	0.44	0.32	41	4.3
$VMgO_x/SiO_2$	165.7	1.69	0.94	10	0.13	0.09	8	12.7
$VMgO_x/Al_2O_3$	158.3	2.47	1.77	19	0.59	0.52	46	4.2
$VMgO_x/ZnO$	17.1	0.25	0.12	21	0.07	0.05	64	3.5

*Calculated from the TCD areas associated with the chemisorption, overall formula: TCD (573–923 K)·100/$_{\mathrm{TCD}\ (373\text{–}923\ \mathrm{K})}$

fashion. Therefore, the high concentration of strong basic centers on the catalyst surface facilitates conversion of CO_2 (acidic molecule). As carbon dioxide adsorbs at the basic sites, the relative acidity of the catalysts surface increases. Consequently, the selectivity to isobutene decreases, whereas the selectivity to isomerization and degradation products increases. This conclusion stays in agreement with our experiments, where the isobutane dehydrogenation in the presence of CO_2 gave lower isobutene selectivity than that in helium atmosphere (table 1).

Figure 2 shows the TPR-H_2 profiles of the tested $VMgO_x$ catalysts. The initial temperature of hydrogen uptake is around 580–660 K for all of the catalysts studied. Moreover, its position increases in the same sequence as T_{max} – the temperature of maximum hydrogen consumption (table 4). Because of extremely high hydrogen uptake over $VMgO_x/C_{act}$, the TPR-H_2 experiments were done for the non-loaded supports (figure 3).

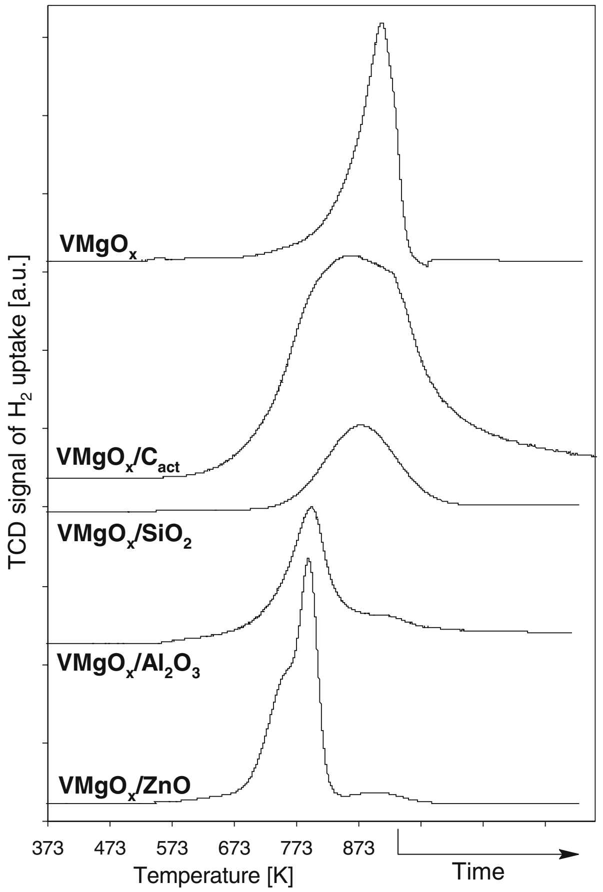

Figure 2. TPR-H_2 profiles of the $VMgO_x$ supported catalysts.

Only two of the supports show positive TCD signal during the TPR-H_2 experiment. ZnO profile shows small hydrogen uptake with the maximum at 673 K, which can be related to some reduction of Zn^{2+} to zinc metal [25]. On the other hand, very high consumption of hydrogen by activated carbon is caused by the chemical nature of the support. It is well known that activation of carbon with oxidizing acids and heating it in carbon dioxide flow yields various oxygen-containing species on its surface. The most important of them are: carboxylic acids and anhydrides, carboxyl-carbonates, lactones, phenols and quinines [26]. Decomposition of oxygen functional groups on carbon surface upon heating in an inert atmosphere has been the subject of many investigations [26–28]. It is well established that thermal treatment of activated carbon at 923 K eliminates almost all of the CO_2-yielding complexes like carboxylic acids, anhydrides and lactones. Despite that, carbon surface still contains an appreciable amount of phenolic and quinolic groups, which have carbon oxide evolution maxima at 900 and 1100 K respectively [26]. These phenomena were confirmed by simple test, where carbon sample was activated in CO_2 flow and outgassed in argon at 923 K. The sample still contained some oxygen groups on the surface, as CO was detected upon further heating of sample at the temperature above 900 K. Despite that, no methane was detected during the temperature-programmed reduction experiment.

Presence of reducible oxygen groups would explain high hydrogen uptake by both activated carbon and carbon-supported $VMgO_x$ catalyst. Consequently, the proper hydrogen consumption by vanadium species (table 4) was calculated as the difference between the H_2 uptake over $VMgO_x$ loaded catalyst and that corresponding to the support.

As the hydrogen consumption by $VMgO_x$ species was similar for all of the supported catalysts, the average oxidation number (n_{av}) of vanadium was established to

Table 4
The results for TPR-H_2 experiments

Sample	T_{max} (K)		H_2 uptake* ($mmol/g_{cat}$)	$(H_2/V)_{mol}$	n_{av}
	Catalyst	Support			
$VMgO_x$	910	–	1.51	0.69	3.6
$VMgO_x/C_{act}$	860	924	0.59	0.57	3.8
$VMgO_x/SiO_2$	877	750	0.38	0.38	4.2
$VMgO_x/Al_2O_3$	797	760	0.43	0.50	4.1
$VMgO_x/ZnO$	792	673	0.57	0.40	3.9

*Calculated from the difference between the H_2 uptake by supported catalysts and the corresponding carrier.

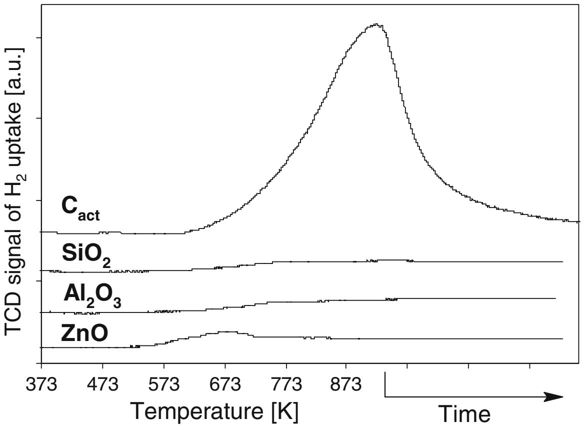

Figure 3. TPR-H_2 profiles of the non-loaded supports.

be around 4. That means that magnesium orthovanadate ($Mg_3V_2O_8$) is reduced on the catalyst surface mainly to Mg_2VO_4. Chang *et al.* [29] proved that reversibility of such reduction is relatively high in the presence of oxygen (7), what is caused by similarity between the structure of both vanadates.

$$2Mg_2VO_4 + \frac{1}{2}O_2 \rightarrow Mg_3V_2O_8 + MgO \qquad (7)$$

As the transformation between the structures requires only a small shift in oxy gen atom positions [29], there is a great possibility for a weak oxidant, such as carbon dioxide, to oxidize the catalyst surface. Such reaction explains the presence of carbon oxide among the products collected during the CO_2 interaction with partially reduced catalyst (table 2).

4. Conclusions

Loading of vanadium magnesium oxide onto SiO_2, Al_2O_3, ZnO and C_{act} afford new catalysts with different performance in the isobutane dehydrogenation reaction. Large surface area of the supported catalysts is not the crucial parameter deciding about their catalytic activity. Much more important are both redox and acid–base properties of the catalysts. Low reducibility of the silica supported $VMgO_x$ causes low isobutane conversion, while its dominating acidic character decides about low conversion of carbon dioxide. Analogously, low acidity and high concentration of strong basic centers on active carbon, alumina and zinc oxide supported catalysts improves the activation of carbon dioxide.

The performed tests show that isobutane dehydrogenation in carbon dioxide atmosphere over $VMgO_x$ catalysts proceed mostly via a two-step pathway. High conversions in the RWGS reaction, especially well seen over alumina and zinc oxide supported catalysts, indicate that the main role of CO_2 is removing hydrogen from the reaction mixture and releasing the thermodynamic limitation of equilibrium. From the other site, the formation of CO in the experiments carried out over coked and partially reduced catalysts indicates that carbon dioxide shows some activity in the catalyst reoxidation and coke gasification reactions at 873 K. Moreover, low activity of the bulk, silica and active carbon supported $VMgO_x$ in RWGS reaction, together with promoting effect of CO_2 in the isobutane dehydrogenation, indicate that one-step pathway of the process cannot be completely excluded. In comparison to Al_2O_3 and ZnO supported samples, the other $VMgO_x$ catalysts are also characterized by slightly higher temperature of maximum hydrogen consumption and lower content of strong acid and basic sites.

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