Nanocrystalline aerogel VO_x/MgO as a catalyst for oxidative dehydrogenation of propane

**Ilya V. Mishakov · Ekaterina V. Ilyina ·
Alexander F. Bedilo · Aleksey A. Vedyagin**

Abstract Nanocrystalline aerogel VO_x/MgO catalysts for the oxidative dehydrogenation of propane with high surface area and uniform vanadium distribution were synthesized by co-gelation followed by supercritical drying. The catalysts were shown to have superior performance compared to nanocrystalline VO_x/MgO catalysts prepared by impregnation.

Keywords VO_x/MgO catalysts · Nanocrystalline oxides · Oxidative dehydrogenation

Introduction

Oxidative dehydrogenation (ODH) of propane is an attractive way to produce propylene. The latter is an important industrial precursor for polymerization processes as well as for the synthesis of propylene oxide, cumene, acetic acid, etc. [1]. Considerable attention has been paid to the development of catalysts with high selectivity to propylene in the ODH. A V/MgO system was found to be one of the best in terms of activity and performance stability [2–4].

Of particular interest are the VO_x/MgO catalysts prepared by impregnation of nanocrystalline MgO aerogel supports with a small crystallite size and high surface area, which are known to have superior adsorption and catalytic properties [5–9]. Such catalysts were shown to be more active in the oxidative dehydrogenation of butane than the VO_x/MgO catalysts prepared in a conventional manner [10–12]. Unfortunately, the impregnation procedure used in these studies [10–12] for the vanadium deposition led to a considerable decrease in the catalyst surface area. In this study, we prepared VO_x/MgO aerogel catalysts by a co-gelation procedure that

I. V. Mishakov (✉) · E. V. Ilyina · A. F. Bedilo · A. A. Vedyagin
Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia
e-mail: Mishakov@catalysis.ru

excludes the impregnation stage, and compared their textural and catalytic properties with those of the catalysts prepared by impregnation.

Experimental

Mixed nanocrystalline V–Mg hydroxides were obtained by an aerogel technique similar to that known for the synthesis of AP–$Mg(OH)_2$ aerogels [5, 6]. This technique starts with dissolving a magnesium ribbon in dry methanol to form a $Mg(OCH_3)_2$ solution. After addition of the gel-stabilizer (toluene), magnesium methoxide was slowly hydrolyzed with distilled water at vigorous stirring. Then, liquid $VO(OC_3H_7)_3$ was added into the formed gel with a syringe. The resulting orange-colored gel was placed into an autoclave and dried under supercritical conditions for removal of solvent at 265 °C and 90 bar to give a mixed V–Mg hydroxide aerogel. Nanocrystalline VO_x/MgO catalysts were obtained by the dehydration of the corresponding aerogel V–Mg hydroxides via their heating in a temperature-programmed regime to 550 °C in a tubular furnace with an intense air flow. The properties of the synthesized catalysts were compared with those of a sample prepared by the impregnation of the nanocrystalline aerogel MgO support synthesized by a similar procedure with an ethanol solution of NH_4VO_3 and also calcined at 550 °C.

The reactivity of the samples in the ODH of propane and the coke deposition kinetics were studied using a gravimetric pulse mass analyzer TEOM 1500 PMA (Thermo Scientific). This instrument allows one to control the sample weight and reaction temperature in a flow reactor with high precision [13]. The weight measurement precision was 5 μg with the maximum measurement frequency as high as 10 points per second. The reaction temperature was varied within the range of 400–600 °C, the reaction gas mixture was 91 vol.% (He) + 4.5 vol.% (O_2) + 4.5 vol.% (C_3H_8). In some experiments, 4.5 vol.% of O_2 was replaced with 9 vol.% of N_2O. The reaction products were analyzed by GC.

Results and discussion

Textural characteristics

According to Table 1, the prepared mixed aerogel V–Mg hydroxides are characterized by very high surface areas exceeding 1000 m^2/g, which are comparable to that of the vanadium-free $Mg(OH)_2$ aerogel prepared by a similar method. The addition of different amounts of vanadium seems to have no significant effect on S_{BET} of the resulting combined hydroxides. However, the subsequent transformation of the aerogel V–Mg hydroxides into corresponding VO_x/MgO catalysts causes a considerable decrease in their surface area to 320–360 m^2/g in a wide range of the vanadium concentrations (Table 1).

Still, this surface area is much higher than those of the catalysts with the similar vanadium loadings but prepared by impregnation of aerogel MgO supports with

Table 1 Specific surface area (S$_{BET}$) of nanocrystalline VO$_x$/MgO samples prepared by the aerogel technique

V concentration, wt% (calculated as V$_2$O$_5$)	S$_{BET}$ (m^2/g)	
	V–Mg-hydroxide (after supercritical drying in autoclave)	VO$_x$/MgO (after dehydration in air at 550 °C)
0	1010	635*
8	1100	325
15	1080	360
27	1050	350

* The sample was dehydrated under vacuum at 500 °C

various vanadium precursors [10–12]. In this study, we compared the catalytic properties of our aerogel VO$_x$/MgO catalysts with those of a catalyst prepared by the impregnation of the aerogel AP–MgO support. After supercritical drying, the Mg(OH)$_2$ aerogel was dehydrated in vacuum at slowly increasing temperature to form AP–MgO with the surface area as high as 635 m^2/g. Unfortunately, after the impregnation of this support with an ethanol solution of NH$_4$VO$_3$ and the following calcination at 550 °C, the surface area of this catalyst was only 160 m^2/g. Still, this value exceeds those reported in the literature for similar materials [10–12].

TEM data

The morphology of the prepared aerogel VO$_x$/MgO samples was studied by high-resolution TEM. According to the TEM data (Fig. 1), the 8%VO$_x$/MgO aerogel catalyst consists mainly of spherical particles 200–300 nm in diameter. Lamellar particles about 100 nm in size are also present. The large agglomerates include the disordered wafer nanoscale (5–6 nm) crystallites of the face-centered cubic and orthorhombic symmetries. As revealed by the EDX analysis, the concentration of vanadium throughout the sample is almost uniform and is close to 4.3 at.%, which corresponds well to the number calculated from the total vanadium concentration. Thus, the developed aerogel method makes it possible to obtain a true nanocrystalline VO$_x$/MgO system with the uniform distribution of the active component (VO$_x$) throughout the support (MgO). In contrast, the traditional preparation method based on impregnating AP–MgO with the V(acac)$_3$ solution gives a non-uniform composition of different magnesium vanadates (ortho- and pyrovanadates) distributed over the surface of aerogel MgO [12].

ODH of propane in the presence of O$_2$

The bar diagram in Fig. 2 demonstrates a sufficient difference in the catalytic activity of the 8%VO$_x$/MgO catalysts prepared either by impregnation of nanocrystalline MgO or by the aerogel method. The sample prepared by the aerogel technique was significantly more active at all the temperatures studied. This difference was especially large at moderate temperatures. For example, the
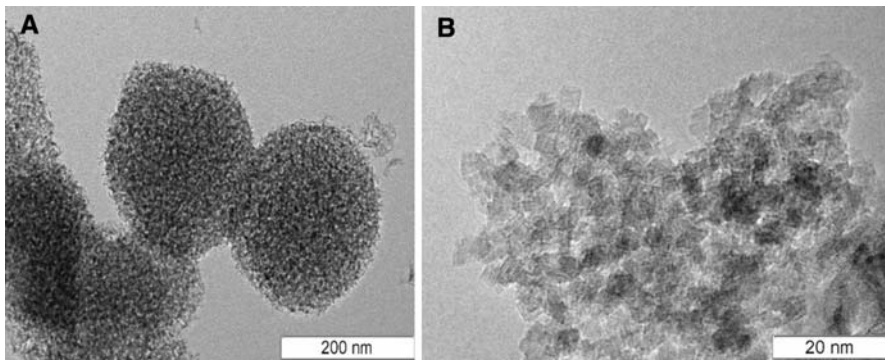
Fig. 1 TEM images of the aerogel 8%VO$_x$/MgO catalyst: globular aggregates (**a**) and primary nanoparticles (**b**)
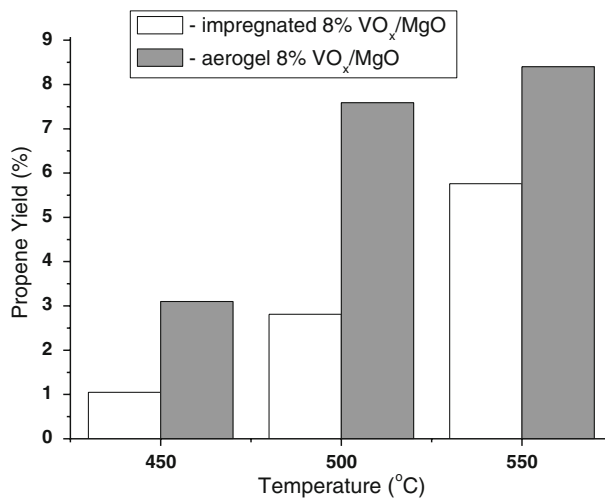
Fig. 2 The yield of propylene in the ODH performed over the 8%VO$_x$/MgO catalyst prepared by impregnation of nanocrystalline MgO (*white bars*) and by the aerogel method (*gray bars*)

propylene yield observed at 500 °C for the aerogel catalyst was almost three times higher than for the impregnated one. It is important that the sample used for comparison was prepared using the nanocrystalline aerogel MgO support and had relatively high surface area. According to the results of earlier studies, such catalysts are more active than those prepared by conventional methods [10–12].

Therefore, the developed aerogel technique provides the synthesis of VO$_x$/MgO catalysts that are substantially more active in the ODH of propane than the catalysts prepared by conventional methods. This effect can be explained by the different distribution of vanadium species in the aerogel and supported VO$_x$/MgO samples and by higher surface area of the former.

ODH of propane in the presence of N$_2$O

Nitrous oxide is another oxidizing agent that can be used for oxidative dehydrogenation. The selectivity benefit of using nitrous oxide instead of oxygen in the ODH of propane is illustrated in Fig. 3. The use of N$_2$O as an oxidizing agent provided the high selectivities towards propylene (85–100%) within the temperature range of 400-500 °C, whereas the use of O$_2$ led to the drop in the selectivity at temperatures above 400 °C, probably due to the enhanced contribution of combustion processes (Fig. 3a). Besides, the selectivity in case of using N$_2$O was higher at all the conversions obtained (Fig. 3b).

Unfortunately, we found that replacement of oxygen by nitrous oxide initiates the undesirable coke formation that leads to catalyst deactivation. The coke deposition was investigated by TEOM in the ODH of propane with N$_2$O. Table 2 shows the amounts of coke deposited during the ODH of propane at 500 °C over aerogel VO$_x$/MgO catalysts under different reaction conditions. It is obvious that the coke is not formed when O$_2$ (4.5 vol.%) is used as the oxidizer. This is evidenced by the constant sample mass during the reaction and the yellowish color of the sample afterwards.

In the experiments with N$_2$O, its concentration was fixed at 9 vol.% in order to keep the C$_3$H$_8$:oxidizer ratio the same. The coke formation rate increased with the vanadia content in the catalyst (Table 2), and for the sample 15%VO$_x$/MgO, the amount of coke deposited reached almost 0.5 wt% after 40 min of the reaction. Besides, after the reaction, the color of the sample turned dark gray or even black, thus confirming the presence of coke on the surface.
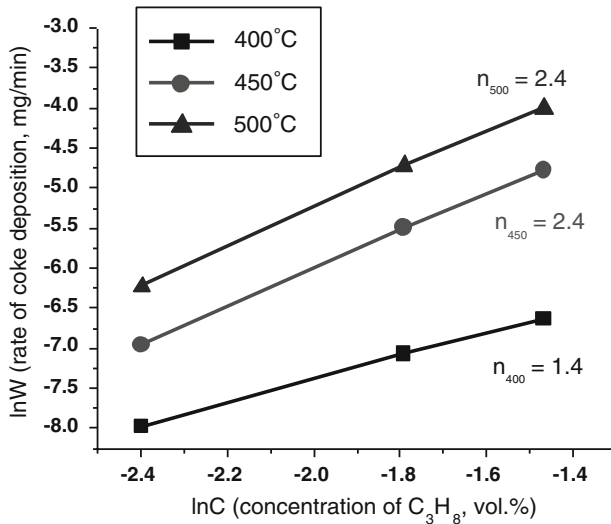
The kinetics of the coke deposition was investigated to evaluate the order of the reaction with respect to propane at different temperatures. For this purpose, the coke deposition rates were measured at various concentrations of propane in the experiments carried out in TEOM over the aerogel 8%VO$_X$/MgO catalyst with the
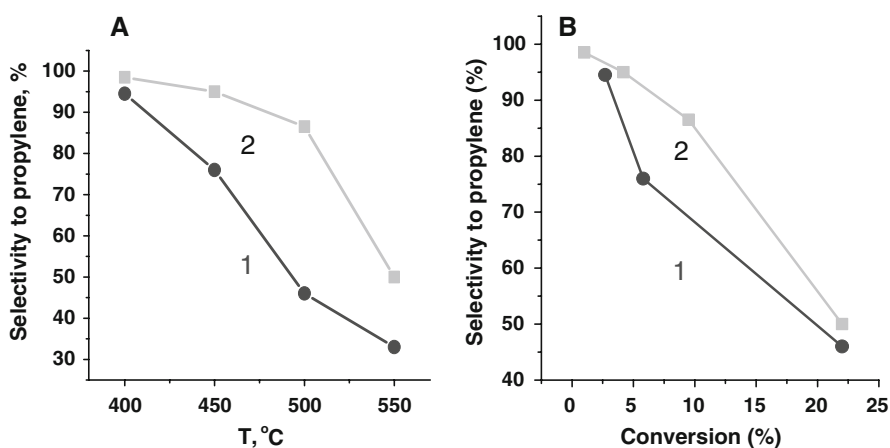
Fig. 3 The dependence of propylene selectivity on temperature (**a**) and propane conversion (**b**) over the aerogel 15%VO$_x$/MgO catalyst using different oxidizing agents: 4.5 vol% O$_2$ (1) and 9 vol% N$_2$O (2)

Table 2 Coke deposition on the VO_x/MgO aerogel catalysts at 500 °C during the ODH of propane with different oxidizing agents

V concentration (wt%) (calculated as V_2O_5)	Amount of coke deposited after 40 min on stream (wt%)	
	4.5 vol.% O_2	9 vol.% N_2O
0	>0.01	0.14
8	>0.01	0.24
15	>0.01	0.49

Fig. 4 The temperature dependence of apparent reaction order (n) for coke formation during the ODH of propane in the presence of N_2O (9 vol%) over the aerogel 8%VO_x/MgO catalyst

feed containing 9 vol.% N_2O. The apparent order (n) for the coke formation appeared to be 1.4 at 400 °C and increased to 2.4 at higher temperatures (450 and 500 °C) (Fig. 4). The obtained high values of the reaction order indicate that the negative effect of coking can be minimized by carrying out the ODH at low propane concentrations.

Thus, aerogel VO_x/MgO samples prepared by co-gelation with subsequent supercritical drying and calcination in dry flowing air at 550 °C proved to have surface areas as high as 360 m^2/g and homogeneous vanadium distribution. Their catalytic activity in the ODH of propane was substantially higher than that of the catalyst prepared by impregnation of the aerogel MgO support. These results suggest that the preparation method developed may be promising for the synthesis of catalysts for the oxidative dehydrogenation.

References

1. Eisele P, Killpack R (1993) Propene. Ullmanns encyclopedia of industrial chemistry. VCH, Weinheim, 211 pp
2. Cavani F, Ballarini N, Cericola A (2007) Catal Today 127:113
3. Klisinska A, Samson K, Gressel I, Grzybowska B (2006) Appl Catal A: General 309:10
4. Balderas-Tapia L, Hernandez-Perez I, Schacht P, Cordova IR, Aguilar-Rios GG (2005) Catal Today 107–108:371
5. Utamapanya S, Klabunde KJ, Schlup JR (1991) Chem Mater 3:175
6. Klabunde KJ, Stark JV, Koper OB, Mohs C, Park DG, Decker S, Jiang Y, Lagadic I, Zhang D (1996) J Phys Chem 100:12142
7. Mishakov IV, Zaikovskii VI, Heroux DS, Bedilo AF, Chesnokov VV, Volodin AM, Martyanov IN, Filimonova SV, Parmon VN, Klabunde KJ (2005) J Phys Chem B 109:6982
8. Mishakov IV, Bedilo AF, Richards RM, Chesnokov VV, Volodin AM, Zaikovskii VI, Buyanov RA, Klabunde KJ (2002) J Catal 206:40
9. Mishakov IV, Heroux DS, Chesnokov VV, Koscheev SG, Mel'gunov MS, Bedilo AF, Buyanov RA, Klabunde KJ (2005) J Catal 229:344
10. Pak C, Bell AT, Tilley TD (2002) J Catal 206:49
11. Chesnokov VV, Bedilo AF, Heroux DS, Mishakov IV, Klabunde KJ (2003) J Catal 218:438
12. Vidal-Michel R, Hohn KL (2004) J Catal 221:127
13. Perez-Ramirez J, Gallardo-Llamas A, Daniel C, Mirodatos C (2004) Chem Eng Sci 59:5535