Journal of Catalysis 260 (2008) 157–163

Contents lists available at ScienceDirect

Journal of Catalysis

www.elsevier.com/locate/jcat

Application of the unique redox properties of magnesium *ortho*-vanadate incorporated with palladium in the unsteady-state operation of the oxidative dehydrogenation of propane

S. Sugiyama [a,b,c,*], Y. Hirata [b], K. Nakagawa [a,b,c], K.-I. Sotowa [a,b,c], K. Maehara [d], Y. Himeno [d], W. Ninomiya [e]

[a] *Department of Advanced Materials, Institute of Technology and Science, The University of Tokushima, Minamijosanjima, Tokushima 770-8506, Japan*
[b] *Department of Geosphere Environment and Energy, Center for Frontier Research of Engineering, The University of Tokushima, Minamijosanjima, Tokushima 770-8506, Japan*
[c] *Department of Chemical Science and Technology, The University of Tokushima, Minamijosanjima, Tokushima 770-8506, Japan*
[d] *Corporate Research Laboratories, Mitsubishi Rayon Co. Ltd., 20-1 Miyuki-cho, Otake, Hiroshima 739-0693, Japan*
[e] *Research and Development Administration Department, Mitsubishi Rayon Co. Ltd., 6-41, Konan 1-chome, Minato-ku, Tokyo 108-8506, Japan*

ARTICLE INFO

Article history:
Received 30 July 2008
Revised 22 September 2008
Accepted 22 September 2008
Available online 15 October 2008

Keywords:
Oxidative dehydrogenation
Propane
Magnesium vanadates
Palladium
Redox
EXAFS
^{51}V MAS NMR
Unsteady-state operation

ABSTRACT

The oxidative dehydrogenation of propane on Pd^{2+}-incorporated magnesium *ortho*-vanadate (Pd-*ortho*-MgVO) was examined, despite the long-held belief that magnesium *ortho*-vanadate ($Mg_3V_2O_8$) demonstrates scant catalytic activity in oxidative dehydrogenation. At 0.75 h on-stream, a higher activity than that on magnesium *pyro*-vanadate (monoclinic $Mg_2V_2O_7$), which is believed to be one of the more active catalysts for oxidative dehydrogenation, was observed using 5% Pd-*ortho*-MgVO. Unfortunately, the higher catalytic activity decreased with time on stream due to the rapid abstraction of lattice oxygen from 5% Pd-*ortho*-MgVO. Although the abstracted lattice oxygen was not regenerated during oxidative dehydrogenation in the presence of excess gaseous oxygen, it was easily regenerated during reoxidation in the absence of propane in the feedstream. Redox cycles of palladium and vanadium species during the catalytic reaction and reoxidation were confirmed using extended X-ray absorption fine structure around the Pd K-edge and ^{51}V magic-angle spinning nuclear magnetic resonance, respectively. The results of the present study suggest that the higher catalytic activity observed using 5% Pd-*ortho*-MgVO at 0.75 h on-stream can be maintained by using an unsteady-state operation in combination with the catalytic reaction and catalyst reoxidation.

1. Introduction

Because some reviews suggest that catalysts containing vanadium species are effective active catalysts for the oxidative dehydrogenation of propane [1–3], various types of vanadium-containing catalysts are still used for the reaction [4–6]. Among vanadium-containing catalysts, magnesium *meta*-, *pyro*-, and *ortho*-vanadates (MgV_2O_6, monoclinic $Mg_2V_2O_7$, and $Mg_3V_2O_8$) are active catalysts for the oxidative dehydrogenation of propane. Magnesium *pyro*-vanadates have the highest activity; *ortho*-vanadates, the lowest activity [1,7]. The ease of removal of the lattice oxygen contained in V=O and/or V–O–V of those magnesium vanadates explains their high catalytic activity in the oxidative dehydrogenation of propane [1,8,9]; however, it should be noted that the structural stability of *pyro*-magnesium vanadate, particularly during the redox cycle, evidently is lower than that of magnesium ortho-vanadate [10]. For example, both monoclinic $Mg_2V_2O_7$ and $Mg_3V_2O_8$ were converted to a mixture of MgO and Mg_2VO_4 during the oxidative dehydrogenation of propane without gaseous oxygen in the feed, indicating that vanadium was reduced from V^{5+} to V^{4+}. When the mixture obtained from monoclinic $Mg_2V_2O_7$ was reoxidized with gaseous oxygen, triclinic $Mg_2V_2O_7$ formed, although not in its original monoclinic phase. The activity of the newly formed $Mg_2V_2O_7$ for the oxidative dehydrogenation of propane was significantly less than that of fresh monoclinic $Mg_2V_2O_7$. In contrast, $Mg_3V_2O_8$ was completely regenerated from the reoxidation of the mixture obtained from $Mg_3V_2O_8$. As a result, the activity for the oxidative dehydrogenation of propane was maintained at a level comparable to that of fresh $Mg_3V_2O_8$. Thus, from a practical standpoint, catalytic activity can be improved by using structurally stable $Mg_3V_2O_8$, rather than structurally unstable monoclinic $Mg_2V_2O_7$.

To control the removal of the lattice oxygen in magnesium vanadates, Ca^{2+}, Cu^{2+}, and Fe^{3+} were incorporated into the magnesium vanadates [11–13]. Catalytic activity certainly is related to the ease of abstraction of the lattice oxygen from the incorporated catalysts; however, the characteristic advantages of the incorpo-

---

[*] Corresponding author at: Department of Advanced Materials, Institute of Technology and Science, The University of Tokushima, Minamijosanjima, Tokushima 770-8506, Japan. Fax: +81 88 656 7432.
E-mail address: sugiyama@chem.tokushima-u.ac.jp (S. Sugiyama).

0021-9517/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2008.09.015

rated cations on catalytic activity, such as enhanced propylene yield, were not observed. This result indicates that a cation that can increase the numbers of mobile lattice oxygen atoms should be examined.

The purpose of the present study was to examine the effect of introducing Pd^{2+} into magnesium ortho-vanadate on the catalytic activity for the oxidative dehydrogenation of propane. Because the Pd^{2+}-incorporated catalysts showed remarkable redox cycle activity in a shorter time-on-stream, our investigation focused on the mobility of lattice oxygen and the redox nature of the palladium and vanadium species using quadrupole mass spectrometry (Q-mass), extended X-ray absorption fine structure (EXAFS) analysis at the Pd K-edge, and ^{51}V solid-state magic-angle spinning nuclear magnetic resonance (^{51}V MAS NMR). Furthermore, to maintain this significantly enhanced activity during a shorter time on stream, an unsteady-state operation combined with the catalytic reaction and reoxidation of the catalyst was investigated using the Pd^{2+}-incorporated catalyst.

2. Experimental

2.1. Catalyst preparation

Magnesium *ortho*-vanadate with Pd^{2+} incorporated (*x*% Pd-*ortho*-MgVO; $x = 100Pd/(Pd + Mg)$ (atomic ratio)) was prepared from $Mg(OH)_2$ (Wako Pure Chemical Industries, Ltd., Osaka, Japan), an aqueous $Pd(NO_3)_2$ solution (24.41% by weight, N.E. Chemcat Corporation, Tokyo, Japan), and NH_4VO_3 (Kanto Chemical Co. Inc., Tokyo, Japan). The preparation procedure was essentially identical to that reported by Sam et al. for the parent magnesium *ortho*-vanadate [7]. An aqueous mixture of a fine powder of $Mg(OH)_2$ and $Pd(NO_3)_2$ was added to an 1% ammonia solution of NH_4VO_3; the reagent amounts were adjusted to the atomic ratios of the corresponding catalysts. The suspension was evaporated under stirring and then dried at 353 K. The resulting solid was ground into a fine powder, calcined at 823 K for 6 h, and then recalcined at 973 K for 10 h. Each solid was finely ground between calcinations. Magnesium *pyro*-vanadate incorporated with Pd^{2+} (5% Pd-*pyro*-$Mg_2V_2O_7$) also was prepared following a procedure similar to that used for the corresponding Pd-*ortho*-MgVO. In the present study, PdO, a mixed catalyst (5% PdO + 95% $Mg_3V_2O_8$), and a supported catalyst (5% Pd/$Mg_3V_2O_8$) also were used. After calcination at 973 K for 3 h, PdO (Wako) was used to test catalytic activity. The mixed catalyst was prepared by mechanical mixing of the calcined PdO and $Mg_3V_2O_8$ prepared in the present study. The supported catalyst was prepared from $Mg_3V_2O_8$ by impregnation of an aqueous $Pd(NO_3)_2$ solution, followed by calcination at 973 K for 3 h.

2.2. Catalytic activity test

The catalyst thus obtained (particles of 0.85–1.70 mm) was used in a fixed-bed continuous-flow reactor operated at atmospheric pressure. Unless stated otherwise, the catalyst was heated to the reaction temperature (723 K) under a continuous flow of helium, then held at this temperature under a 25 mL/min flow of oxygen for 1 h. Typical reaction conditions were $W = 0.5$ g, $P(C_3H_8) = 14.4$ kPa, $P(O_2) = 4.1$ kPa, and $F = 30$ mL/min; equilibration to atmospheric pressure was provided by helium. No homogeneous oxidation of propane was observed under the study conditions. The reaction was monitored by a online gas chromatograph with a thermal conductivity detector (GC-8APT, Shimadzu, Kyoto, Japan). The conversion of propane was calculated from the products and the propane introduced into the feedstream. The selectivity was calculated from the conversion of propane to each product on a carbon basis. The carbon mass balance was $100 \pm 5\%$. The reaction rate per unit of surface area was estimated as the rate ($r = FC_0X_A/W$, where F, C_0, X_A, and W were the flow rate, initial concentration of C_3H_8, conversion of C_3H_8 and catalyst weight, respectively) per catalyst surface area [14]. For continuous analysis of the reaction, an effluent gas from the reactor was introduced into the Q-mass (Pfeiffer OmniStar-s, Hakuto Co., Tokyo, Japan).

2.3. Characterization

The catalysts were characterized using X-ray diffraction (XRD; RINT 2500X using monochromatized Cu$K\alpha$ radiation, Rigaku Co., Tokyo, Japan). X-ray photoelectron spectroscopy (XPS; ESCA-1000AX, Shimadzu) was performed using Mg$K\alpha$ radiation. ^{51}V MAS NMR spectra were obtained using an Avance DSX300 (Bruker BioSpin K. K., Osaka, Japan) with an external reference of 0.16 M $NaVO_3$ (Wako) solution at −574 ppm at room temperature and a spinning rate of 25 kHz. Specific surface areas were calculated from adsorption isotherms obtained with a conventional BET nitrogen adsorption apparatus (BELSORP-18SP, Bell Japan, Inc., Osaka, Japan). Analysis of EXAFS near the Pd K-edge was carried out at the High-Energy Research Organization with a storage ring current of approximately 400 mA (6.5 GeV). The X-ray was monochromatized with Si(311) at an NW-10A station. The absorption spectra were observed using ionization chambers in transmission mode. Samples containing palladium species were diluted with BN (Wako) and compressed to a diameter of 13 mm. The photon energy was scanned in the range of 24,080–25,600 eV for a Pd K-edge. The EXAFS data were analyzed using the EXAFS analysis program REX (Rigaku). Fourier transformation of k^3-weighted EXAFS oscillation was performed in the range of 0.4–1.6 nm^{-1}. Inverse Fourier-transformed data for Fourier peaks were analyzed using a curve-fitting method, with phase shift and amplitude functions derived from FEFF 8.0 [15].

3. Results and discussion

3.1. Catalytic activities on Pd-ortho-MgVO

Four types of Pd-*ortho*-MgVO were prepared. The XRD pattern of the undoped catalyst was essentially identical to the reference pattern of $Mg_3V_2O_8$ (JCPDS 37-0351) (Fig. 1A), whereas those of the three Pd-*ortho*-MgVO were matched to the mixture of $Mg_3V_2O_8$ and PdO (JCPDS 41-1107) (Figs. 1B–1D). It should be noted that the intensity of the PdO signal increased with increasing Pd content.

Fig. 2 shows the time course of the propylene yields for various Pd-*ortho*-MgVO. Table 1 gives the conversion, selectivity, reaction rate per unit of surface area, and surface area. Although the C_3H_6 yield decreased significantly with time-on-stream, the yield increased with Pd loading, particularly at the initial time-on-stream. At 0.75 h on-stream, the propylene yields were 5% Pd-*ortho*-MgVO (7.8%) > *pyro*-$Mg_2V_2O_7$ (7.1%) [12] > *ortho*-$Mg_3V_2O_8$ (2.9%). These results show that incorporation of the Pd^{2+} species into $Mg_3V_2O_8$ resulted in enhanced activity for the oxidative dehydrogenation of propane under equivalent reaction conditions. However, as shown in Fig. 1, PdO and $Mg_3V_2O_8$ were detected in Pd-*ortho*-MgVO using XRD. Therefore, either PdO itself or the synergistic effects of the combination of PdO and $Mg_3V_2O_8$, in bulk or on the surface, may contribute to the enhanced initial activity on Pd-*ortho*-MgVO. Furthermore, vanadate may be present on the surface of $Mg_3V_2O_8$ as a supported catalyst. Consequently, the activities on PdO and on the binary oxides, 5% PdO and 95% $Mg_3V_2O_8$ (by weight), together with that on the supported catalyst (5% Pd/$Mg_3V_2O_8$), were examined (Fig. 3 and Table 1). As shown in Fig. 3, relatively stable and low activity was observed on both PdO and binary oxides. In particular, the yield of C_3H_6 on PdO was about 25% of that on 5% Pd-*ortho*-MgVO, while that on the binary oxide was almost the