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A Raman Spectroscopy Study of Alumina-Supported Vanadium Oxide Catalyst during Propane Oxidative Dehydrogenation with Online Activity Measurement

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The use of an advanced *in situ* methodology that combines *in situ* Raman spectra during catalytic operation and simultaneous online activity measurement is used to study the performance and structure of supported vanadium oxide catalysts during propane oxidative dehydrogenation (ODH). *In situ* spectroscopy during reaction conditions, with online activity measurement, comprises the simultaneous use of both catalytic and spectroscopic measurement on the same sample. Thus, the possibility of assessing a structure–activity relationship at a molecular level becomes reliable since the structures observed correspond to the working catalyst, as determined online. It is shown that the structure of supported vanadium oxide catalyst under propane ODH is close to that of the system under dehydrated conditions but may show a very moderate extent of reduction. The extent of reduction is strongly dependent on the O_2/C_3H_8 ratio in the reaction feed. Raman spectroscopy during reaction conditions with online activity measurement shows that surface polymeric vanadium oxide species are more reducible than isolated surface polymeric species. The reduction of surface polymeric species decreases moderately the conversion values but has no appreciable effect on the conversion and selectivity values during propane ODH reaction. Therefore, the active site for propane ODH reaction on alumina-supported vanadia must be a single VO_4 site, and no special arrangement of V sites appears to be critical. It is also discussed that the V–O–V bond may not be critical for this reaction.

Key Words: **reaction *in situ*; Raman–GC; propane ODH; vanadia; alumina; active site; structure–activity relationship.**

INTRODUCTION

The ODH routes represent the most promising emerging technology being investigated to convert light alkane feeds to their respective valuable olefin counterparts. ODH routes are being targeted for the use of an oxidant to make the process exothermic. However, ODH routes have several technical challenges to overcome before they become commercially viable. These challenges are identifying highly activity catalysts and controlling the heat of reaction generated. In particular, the assessment of the structure–activity/selectivity relationship at a molecular level would allow a more efficient design of better catalysts. In this line, supported metal oxide catalysts show interesting performance for selective oxidation of light alkanes toward olefins and O- or N-containing products (1–5).

Vanadium oxide is a major component in the formulation of catalysts for selective oxidation reactions (1–5). The activity of supported vanadium oxide catalysts is strongly affected by the interaction with the specific oxide support and by the textural and chemical properties of the oxide support (1, 2). The surface coverage of the vanadium oxide also influences the structure and activity of the catalysts because it affects the polymeric-to-monomeric population ratio of the supported vanadium oxide species. The role of surface isolated and polymeric vanadia species in the oxidation of light paraffins is under study (6–8). Both parameters may determine the amount and nature of exposed oxygen sites that interact with the hydrocarbon molecule.

The need to assess a reliable structure–activity/selectivity relationship at a molecular level requires the knowledge of the structure of the active site during catalytic operation. There have been a number of *in situ* studies which characterize the catalysts under conditions similar to those ruling in catalytic processes (9–17). However, the use of an advanced *in situ* spectroscopy that looks at the catalyst structure under real reaction conditions appears critical to providing the most accurate structure-activity/selectivity relationship understanding. In this line, *in situ* Raman spectroscopy during catalytic operation with online activity measurement is being introduced (18–20). It has been proposed that the *in situ spectroscopic study with simultaneous online activity measurement* be named "o*perando*" (working, in Latin) spectroscopy for the sake of simplicity (18–21). This contribution applies this methodology to the study of alumina-supported vanadia for propane ODH.

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EXPERIMENTAL

The Raman spectra during propane ODH were run with a Renishaw Micro-Raman System 1000 equipped with a cooled CCD detector (−73°C) and a holographic supernotch filter that removes the elastic scattering. The samples were excited with the 514-nm Ar line. The spectra acquisition consisted of five accumulations of 60 s for each sample. The Raman spectra during propane ODH were run with a homemade reaction cell that consists of a fixed-bed quartz microreactor contained by quartz wool plugs on both ends. The microreactor walls have optical quality. The cell was heated to reaction temperature and the gas feed and outlet was heated so that there were no cold points in the way from the Raman–GC cell to the online gas chromatograph. The catalyst (V–Al) was prepared by impregnation of γ-Al_2O_3 (160 $m^2\ g^{-1}$) support with an ammonium metavanadate aqueous solution. The content of vanadium in the catalyst corresponded to a 0.5-monolayer coverage of VO_x, i.e., nearly 4 V atoms/nm^2 (16% V_2O_5). Propane oxidation ($C_2H_6/O_2/He = 1/2/8$) was performed with a total flow rate of 67 cm^3/min and 150 mg of catalyst. Activity data from the fixed-bed conventional reactor and the Raman–GC cell showed no significant differences. During the Raman–GC study, the catalyst structure and its performance were analyzed (Raman and online GC) every 10°C. Several Raman and GC analyses were run at each temperature. To prevent local heating on the sample due to the laser beam during the acquisition, the laser power was low (8 mW). Acquisition time was 200 s. Thus, the spectra were taken at representative spots, with no appreciable heating with respect to the reaction temperature. The GC analyses were run in a HP-5980-Series II gas chromatograph with a TCD detector and automatic online sampling through a six-way valve. The analytic system was composed of two columns, Porapak-Q and Molecular Sieve 4A, in a column-isolation configuration.

RESULTS

The conversion of propane to the different products in the Raman–GC reaction cell is illustrated in Fig. 1. As, expected, both propane and oxygen conversion values increase with reaction temperature. The conversion of propane shows a moderate increase with O_2/C_3H_8 molar ratio in the reaction feed; however, this is a minor change. The conversion of oxygen decreases with O_2/C_3H_8 molar ratio. The decrease in oxygen conversion with O_2/C_3H_8 molar ratio is consistent with an increasing excess of oxygen.

The selectivity vs conversion profiles for propylene, CO, and CO_2 at different O_2/C_3H_8 molar ratios is presented in Figs. 2A–2C, respectively. The O_2/C_3H_8 molar ratio does not have any appreciable effect on the selectivity trends during propane ODH on alumina-supported vanadia catalysts.

The dehydrated catalyst exhibits Raman bands at 1026 and 1009 cm^{-1} (Fig. 3A). These bands correspond to the terminal V=O bond of surface isolated and surface polymeric vanadium oxide species, respectively. The total intensity of the Raman bands cannot be quantified, since there is need of an internal reference. However, it is possible to follow the relative intensities of these two Raman bands vs reaction conditions. The surface polymeric vanadia species (Raman band at 1009 cm^{-1}) disappear at 370°C when the O_2/C_3H_8 molar ratio in the reaction feed is 2, while no appreciable changes are observed for the Raman band at 1026 cm^{-1}. Under these conditions, the catalyst achieves 5.6% conversion of propane, as determined by online GC. As the reaction temperature increases, conversion increases up to 11.3% at 400°C with no appreciable changes in the Raman band at 1026 cm^{-1}. When the O_2/C_3H_8 molar ratio is 6 (Fig. 3B), the catalyst shows both Raman bands at 1026 and 1009 cm^{-1}. The Raman band corresponding to the V=O terminal bond of surface polymeric vanadia species (1009 cm^{-1}) is present at temperatures higher than those observed when the O_2/C_3H_8 molar ratio is 2, and it

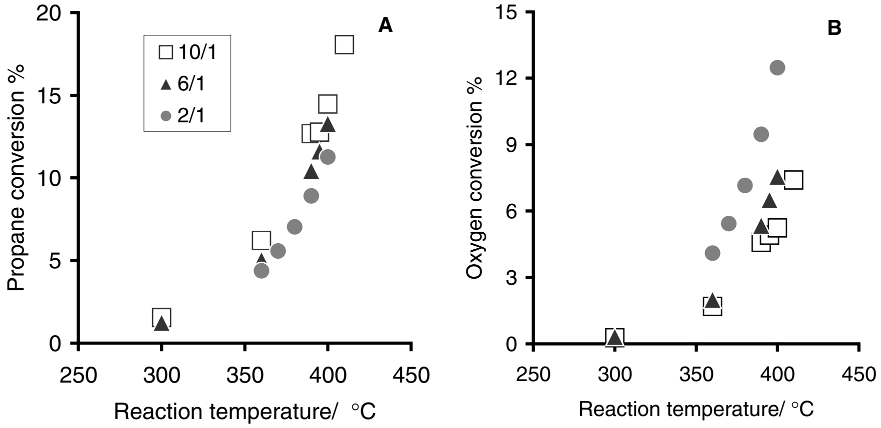

FIG. 1. Propane and oxygen molar conversion in the reaction *in situ* Raman–GC cell during spectroscopic study of propane ODH of VO_x/Al_2O_3 catalyst vs reaction temperature at different O_2/C_3H_8 molar ratios. The corresponding simultaneous Raman spectra during propane ODH are shown in Figs. 3 and 4.

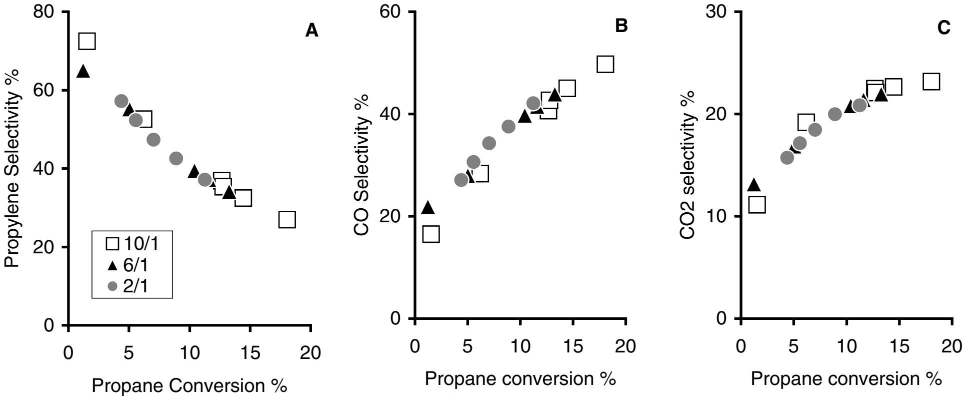

FIG. 2. Selectivity vs propane conversion profiles for propylene (A), carbon monoxide (B), and carbon dioxide (C) in the *in situ* Raman–GC reaction cell during the study of propane ODH of VO_x/Al_2O_3 catalyst. The corresponding simultaneous Raman spectra during propane ODH are shown in Figs. 3 and 4.

is evident at 410°C (16.5% propane conversion) (Fig. 3B). The results with an O_2/C_3H_8 molar ratio of 10/1 are equivalent to those shown in Fig. 3B. A comparison of catalyst V–Al at 400°C and under O_2/C_3H_8 molar ratio of 2/1, 6/1, and 10/1 is illustrated in Fig. 4. No appreciable effect is recorded on the molecular structures of surface vanadium oxide species as the O_2/C_3H_8 molar ratio decreases from 10/1 to 6/1. Both surface isolated (V=O mode at 1026 cm^{-1}) and surface polymeric (V=O mode at 1009 cm^{-1}) vanadium oxide species show essentially the same relative intensity. However, the catalyst V–Al exhibits only the Raman band at 1026 cm^{-1} when the O_2/C_3H_8 molar ratio decreases to 2/1 (Fig. 4A). However, the catalytic performance recorded simultaneously shows negligible changes, as illustrated in the conversion and selectivity values measured online (Fig. 4B).

DISCUSSION

The results presented above show that the change in O_2/C_3H_8 ratio has a moderate effect on O_2 conversion and

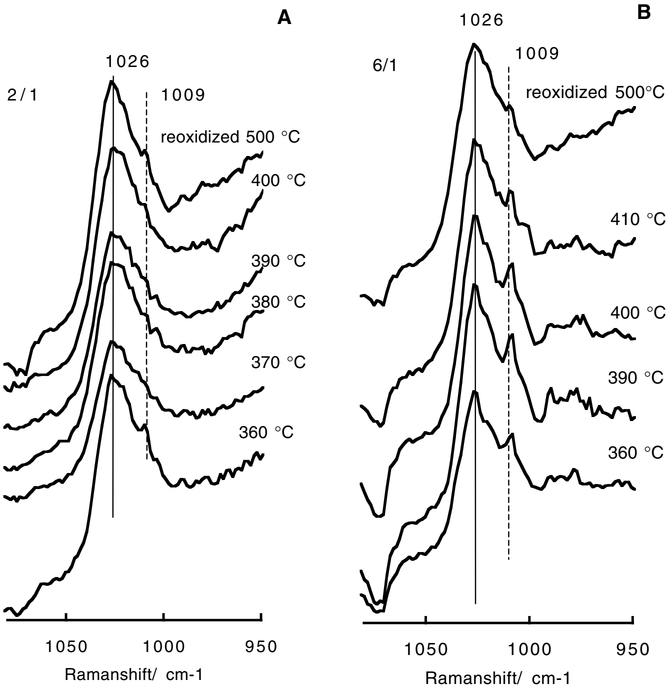

FIG. 3. Raman spectra of VO_x/Al_2O_3 catalyst during propane ODH vs reaction temperature in the reaction *in situ* Raman–GC cell during spectroscopic study of propane ODH at O_2/C_3H_8 molar ratios of 2 (A) and 6 (B). The corresponding simultaneous activity data are illustrated in Figs. 1 and 2.

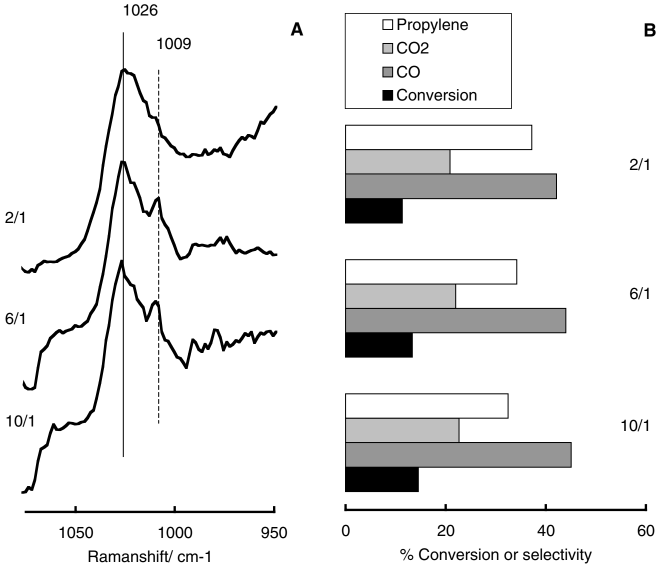

FIG. 4. Raman spectra of VO_x/Al_2O_3 catalyst during propane ODH vs O_2/C_3H_8 molar ratio at 400°C reaction temperature in the *in situ* Raman–GC reaction cell during spectroscopic study of propane ODH (A) and conversion of propane and selectivity to CO, CO_2, and propylene analyzed online (B).

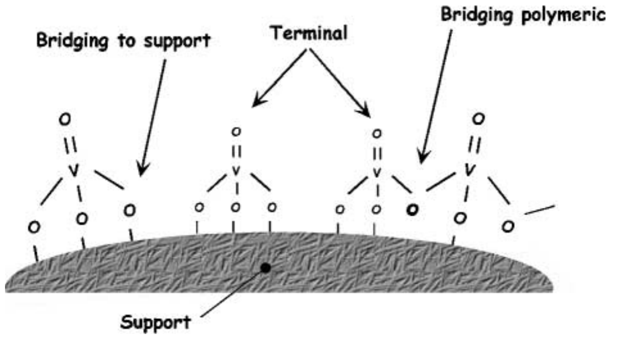

FIG. 5. Scheme of surface isolated and surface polymeric vanadium oxide species.

a minor effect on propane conversion. This trend agrees with the kinetic order zero for oxygen partial pressure and with isotopic studies for propane oxidation on VO_x/ZrO_2 (22, 23). The selectivity–conversion profiles do not appear to be affected when the O_2/C_3H_8 molar ratio increases (Fig. 2). However, Raman spectra during propane ODH show structural effects of the O_2/C_3H_8 molar ratio on the molecular structures of surface vanadium oxide species. Surface polymeric vanadium oxide species reduce at low O_2/C_3H_8 molar ratio values. The higher reducibility of surface polymeric vanadia species is in agreement with previous studies using *in situ* Raman and *in situ* UV–vis spectroscopy (2, 24–26). The loss of surface polymeric species does not result in a breakdown of catalyst activity or selectivity.

There is a controversy about which oxygen site is related to the active center in oxide catalysts (Fig. 5). The terminal metal–oxygen double bond has been proposed as the active site for selective oxidation of hydrocarbons; however, INDO calculations suggest that the interaction of a hydrocarbon molecule is most favorable with a bridging oxygen than with a terminal one for vanadium oxide clusters (27). The position of the V=O band does not correlate with the changes of activity of the catalysts for ethane ODH, for butane oxidation, or for methanol oxidation (28–30). Combined *in situ* Raman and isotopic labeling studies show that the bridging oxygen sites are involved in the selective oxidation of hydrocarbons on β-$VOPO_4$ and bismuth molybdates (31, 32) and that the terminal $V{=}^{18}O$ bond is stable for several characteristic reaction time cycles during hydrocarbon oxidation on supported metal oxide catalysts (25, 33). The present study shows that disappearance of some terminal V=O bonds have no effect on the activity and selectivity of VO_x/Al_2O_3 catalyst. All these results rule out the terminal V=O bond as the critical active site of supported vanadium oxide catalysts for the oxidation of propane. Thus, bridging oxygen sites appear to be the active sites. There are two possible active bridging oxygen sites: those binding the supported vanadia to the support (V–O–S) and those binding surface polymeric vanadia species (V–O–V).

In the present study, the role of isolated vs surface polymeric vanadia species can be evaluated, and therefore, the role of V–O–V bonds vs V–O–Al bonds can be evaluated. The polymeric-to-isolated ratio in surface vanadia species increases with coverage on the oxide support. Alumina coverage in the reported V-Al catalyst is half a monolayer (4 V atoms/nm^2) and the polymeric-to-isolated surface vanadia species must be rather low. Thus, the moderate decrease of propane conversion values as the O_2/C_3H_8 molar ratio decreases may reflect the loss of active sites associated with polymeric species (V–O–V bond). However, the loss of polymeric surface vanadium oxide species has no effect on the selectivity–conversion profiles for propane ODH on VO_x/Al_2O_3 catalysts. The constancy of catalytic performance of VO_x/Al_2O_3 catalysts with an O_2/C_3H_8 molar ratio demonstrates that the nature of the active site for propane ODH reaction is not affected by the loss of polymeric surface vanadia species. Thus, propane ODH on alumina-supported vanadia requires not a special coordination of sites to be active but a single site.

CONCLUSION

Raman spectra during propane ODH with online GC activity analysis allows the simultaneous knowledge of the activity and molecular structures and catalytic performance of alumina-supported vanadium oxide catalysts for propane ODH. This methodology shows that the O_2/C_3H_8 molar ratio has a weak effect on the activity and no appreciable effect on the selectivity of alumina-supported vanadium oxide catalysts during propane ODH. The partial reduction of surface vanadium oxide species is due to a preferential reduction of the polymeric surface vanadium oxide species when the O_2/C_3H_8 molar ratio decreases. The selectivity profiles of VO_x/Al_2O_3 catalyst are not affected by the loss of polymeric surface vanadia species. Thus, propane ODH does not require a special coordination of vanadia sites.

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