JOURNAL OF CATALYSIS **158,** 349–353 (1996)
ARTICLE NO. 0034

# NOTE

# Selective Oxidation of Pentane over $Al_2O_3$- and $SiO_2$-Supported Vanadia Catalysts

Selective oxidation of light alkanes has been a research subject of continual interest because of their potential industrial applications. The results of these studies show that the product selectivity depends both on the alkane and the chemical composition, the phases, and the cation oxidation state of the catalyst. For example, a recent summary of the product distributions in the oxidation of $C_2$ to $C_6$ alkanes over $Mg_3(VO_4)_2$, $Mg_2V_2O_7$, and VPO (vanadyl pyrophosphate) catalysts (1) shows that the primary reaction pathway, oxidative dehydrogenation, formation of oxygen-containing organic products, or combustion to carbon oxides, depends not only on the local environment of the vanadium–oxygen unit in the catalyst, but also on the size of the alkane. Similarly, the selectivity pattern in butane oxidation on $V_2O_5$ supported on $SiO_2$ (2) or $\gamma$-$Al_2O_3$ (3) depends on vanadia loading. Lower loading catalysts are more selective to dehydrogenation products. It was suggested that the vanadia species present in both the low-loading $SiO_2$- and $Al_2O_3$-supported samples are difficult to reduce and consequently have few reactive lattice oxygen atoms available to oxidize surface hydrocarbon intermediates.

In the studies of butane oxidation over supported vanadium oxides mentioned above, carbon oxides, butenes, and butadiene accounted for almost all of the reaction products, with only small amounts (less than 10%) of oxygenated products. Since the formation of oxygenated products probably involves the participation of lattice oxygen, it should depend also on the reducibility of the cations. It has been reported that oxygenates were formed in the oxidation of pentane over VPO, 12-molybdophosphoric acid, vanadomolybdophosphates, and vanadium-substituted molybdophosphoric acid. In particular, both maleic anhydride and phthalic anhydride were formed with high selectivities on VPO (4–6), whereas maleic anhydride was formed on the heteropoly acids (7, 8). Therefore, it seems that the oxidation of pentane can be used to further study the variation of selectivity on supported vanadia catalysts. Here, we report the results of such a study on vanadia catalysts supported on $SiO_2$ and $\gamma$-$Al_2O_3$.

The preparation of $V/SiO_2$ (2) and $V/\gamma$-$Al_2O_3$ (9) have been described previously. The $SiO_2$ used was washed with dilute acid to remove metal ion impurities. Vanadia was introduced by impregnating $Al_2O_3$ with a methanol solution of vanadium triisopropoxide, or by impregnating $SiO_2$ with an aqueous oxalic acid solution of ammonium metavanadate. The vanadia loadings for the $Al_2O_3$ samples were 8.2 and 23.4 wt% $V_2O_5$ and for the $SiO_2$ samples were 1 and 10 wt%. They will be denoted as 8.2 VAl, 23.4 VAl, 1VSi and 10 VSi, respectively. The surface area of $Al_2O_3$ was 181 $m^2/g$, whereas those of 1VSi and 10VSi were 300 and 260 $m^2/g$, respectively. Catalytic reactions were conducted over these samples in a fused silica, tubular flow reactor in a system similar to those described previously (2). Control experiments were conducted to ensure that there was no contribution from the homogeneous reaction in the data reported. The reaction products were analyzed by gas chromatography using a combination of columns: VZ-7 (Alltech), Carbosphere (Alltech), and Chromosorb (Alltech) (10).

The steady state product distributions in the oxidation of pentane over these catalysts are shown in Table 1. The $Al_2O_3$-supported catalysts were substantially more active than the $SiO_2$-supported ones, as indicated by the much lower reaction temperature used for these samples. For samples of the same support, the activity per mole of vanadium depended only weakly on the loading. However, the selectivity patterns depended strongly on the support and the vanadia loading. At low pentane conversions, 1VSi produced primarily pentenes and 1,4-pentadiene whereas 10VSi produced primarily carbon oxides and some maleic anhydride. On the $Al_2O_3$-supported samples, no dehydrogenation products were observed. Maleic anhydride was produced with a selectivity of about 80% at low conversions on 23.4VAl, but was a minor, though still substantial, product on 8.2VAl. Since the highest carbon-based selectivity for the formation of a four-carbon maleic anhydride molecule from a five-carbon pentane molecule is 80%, the high selectivity observed on 23.4VAl at low conversions implied that maleic anhydride is the only initial product on this catalyst, and the lower selectivities at higher conversions are due to further oxidation of maleic anhydride. Only small amounts of phthalic anhydride was observed on the $Al_2O_3$-supported samples, and none was observed on the $SiO_2$-supported samples.

The differences between the $SiO_2$-supported and the

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**TABLE 1**

**Steady State Reaction Data for Pentane Oxidation[a]**

| Catalyst | Wt (g) | Flow rate (ml/min) | Activity, $10^{-4}$ mol $C_5$ (mol V-min)$^{-1}$ | T (°C) | C5 conv. (%) | Product selectivity (%[b]) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $C_5$ = | $tC_5$ = | $cC_5$ = | MA | PA | CO | $CO_2$ | oth. |
| 8.2VAl | 0.47 | 39 | 0.3 | 225 | 1 | 0 | 0 | 0 | 28 | 7 | 58 | 0 | 7 |
| | | | 3.3 | 260 | 11 | 0 | 0 | 0 | 14 | 2 | 51 | 30 | 3 |
| | | | 9.2 | 300 | 31 | 0 | 0 | 0 | 8 | 1 | 56 | 35 | 2 |
| | 0.32 | 40 | 8.1 | 300 | 18 | 0 | 0 | 0 | 14 | 0 | 50 | 34 | 0 |
| | 0.22 | 40 | 5.9 | 300 | 9 | 0 | 0 | 0 | 17 | 2 | 46 | 32 | 3 |
| 23.4VAl | 0.050 | 35 | 3.5 | 300 | 4 | 0 | 0 | 0 | 53 | 4 | 25 | 19 | 0 |
| | | 42 | 2.1 | 300 | 2 | 0 | 0 | 0 | 76 | 3 | 3 | 18 | 0 |
| | | 80 | 34 | 400 | 17 | 0 | 0 | 0 | 38 | 2 | 28 | 29 | 0 |
| | | 35 | 40 | 400 | 46 | 0 | 0 | 0 | 14 | 0 | 44 | 42 | 0 |
| | 0.105 | 97 | 22 | 300 | 19 | 0 | 0 | 0 | 41 | 0 | 28 | 29 | 2 |
| | | 43 | 12 | 300 | 23 | 0 | 0 | 0 | 36 | 0 | 32 | 30 | 2 |
| | | 34 | 10 | 300 | 25 | 0 | 0 | 0 | 31 | 0 | 34 | 33 | 1 |
| 23.4VAl + $Al_2O_3$[c] | | 34 | 7 | 300 | 17 | 0 | 0 | 0 | 0 | 0 | 47 | 53 | 0 |
| 1VSi | 1.5 | 200 | 8 | 425 | 2 | 32 | 41 | 24 | 0 | 0 | 0 | 0 | 3 |
| | | 100 | 10 | 425 | 5 | 25 | 27 | 16 | 0 | 0 | 14 | 14 | 4 |
| | | 50 | 12 | 425 | 12 | 20 | 20 | 12 | 0 | 0 | 20 | 23 | 5 |
| | | 25 | 13 | 425 | 26 | 15 | 15 | 8 | 0 | 0 | 27 | 31 | 5 |
| 10VSi | 0.1 | 220 | 19 | 425 | 3 | 3 | 0 | 0 | 23 | 0 | 42 | 30 | 3 |
| | | 92 | 19 | 425 | 7 | 1 | 0 | 0 | 27 | 0 | 42 | 28 | 2 |
| | | 50 | 16 | 425 | 11 | 1 | 1 | 1 | 26 | 0 | 39 | 31 | 1 |

[a] Feed composition: $C_5H_{12}/O_2/He = 4/8/88$.

[b] $C_5$ =: 1-pentene, $tC_5$ =: *trans*-2-pentene, $cC_5$ =: *cis*-2-pentene, MA: maleic anhydride, PA: phthalic anhydride, oth.: acetic acid, propanoic acid, propene, and ethene.

[c] 1g $Al_2O_3$ placed after 0.105 g 23.4VAl.

$Al_2O_3$-supported samples were not due to different reaction temperatures. On 23.4VAl, the selectivities for maleic anhydride at 17–19% pentane conversions varied little over the temperature ranging from 300 to 400°C (Table 1). $\gamma$-$Al_2O_3$ was not active in pentane oxidation, yielding a conversion of only 1% at 300°C over 1 g of sample and with a feed flow rate of 34 ml/min. However, when 1 g of $Al_2O_3$ was placed behind a bed of 23.4VAl, the maleic anhydride produced was completely combusted to carbon oxides. Since a monolayer coverage corresponded to about 27 wt% vanadia on this $\gamma$-$Al_2O_3$ (9), the 8.2VAl sample had a large fraction of exposed alumina surface, which undoubtedly contributed to the lower selectivity for partial oxidation products observed on this sample than that observed on 23.4VAl. On the other hand, a bed of silica was found to be inert toward combustion of maleic anhydride. Thus, the low selectivity for maleic anhydride over 10VSi was not due to degradation over exposed silica.

The dependence of product selectivity in pentane oxidation on vanadia loading was similar to that observed in butane oxidation on the same catalysts. In butane oxidation, the lower loading $SiO_2$-supported sample yielded a significantly greater quantity of butenes and butadiene than the higher loading sample (2). Very little maleic anhydride was detected for either loading. On the $Al_2O_3$-supported sample, dehydrogenation was also more predominant on the lower loading sample, but about 13% maleic anhydride was detected at 8% butane conversion over the higher loading sample (3). These trends were also evident in the data in Table 1. Higher yields of oxygenates were observed on the $Al_2O_3$-supported samples, and the highest yield of dehydrogenation products was observed on the lower loading $SiO_2$-supported sample.

There was evidence that the higher loading samples were reduced during steady state reaction. The 1VSi sample was white in color when it was cooled in the reaction mixture. However, the 10VSi was black, versus reddish orange before reaction, and turned blue and then green upon exposure to air. This latter change in color was consistent with reoxidation of the vanadium ions toward $V^{5+}$. The 23.4VAl sample also changed from yellow to black after reaction, and to green after standing in air at room temperature.

Spectroscopic characterization of the samples also suggested reduction of the vanadium ions in the higher loading samples under reaction conditions. Raman spectra of 10VSi after reaction could only be obtained after treating

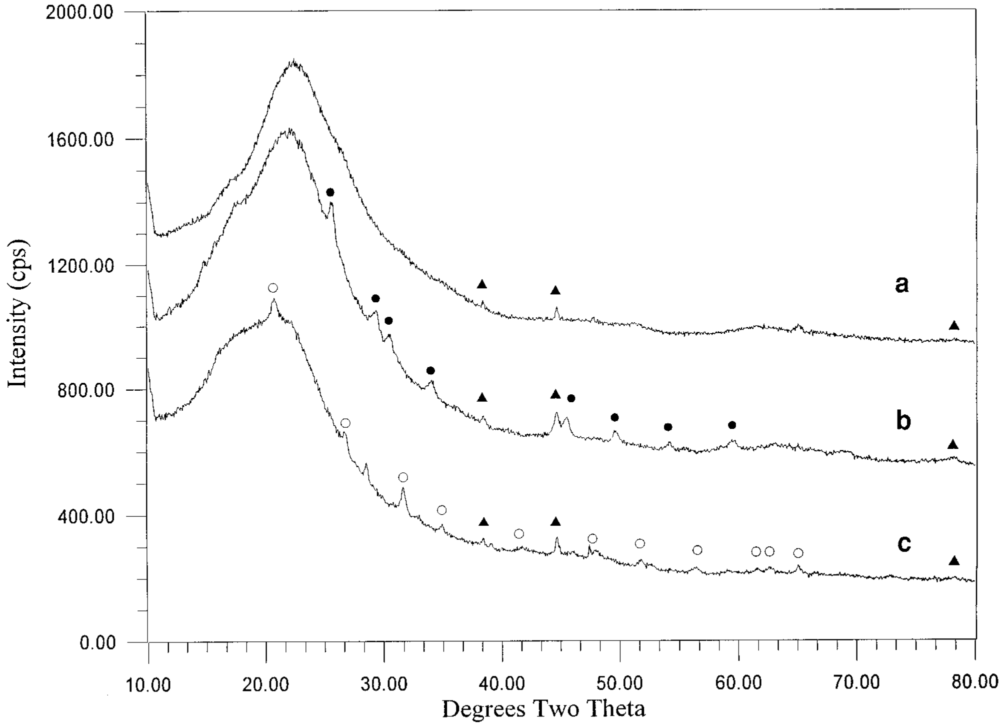

**FIG. 1.** XRD patterns of 10VSi (a) before reaction, (b) after reaction, and (c) after reaction and then reoxidized in oxygen. ($VO_2 \cdot xH_2O$: ●, $V_2O_5$: ○, Al sample holder: ▲)

the sample in oxygen at 500°C. The X-ray diffraction pattern of 10VSi after reaction showed peaks attributable to $VO_2 \cdot xH_2O$ (Fig. 1). After reoxidizing the sample in oxygen, peaks of $V_2O_5$ were detected. The Raman spectrum of the used and then reoxidized sample showed intense peaks of $V_2O_5$ (at 998 and 703 $cm^{-1}$) that were much more prominent than in the spectrum of the fresh 10VSi sample (Fig. 2 curves a and b). Thus, the vanadia species agglomerated into crystallites and were in a reduced state under reaction conditions. In contrast, there were no detectable differences between the spectrum of a fresh and an used 1VSi sample, which showed the 1040 $cm^{-1}$ peak of isolated vanadyl species. This difference between the behavior of the 10VSi and the 1VSi samples has been reported in butane oxidation also (2).

The Raman spectrum of unused and dry 23.4VAl showed a vanadyl peak at about 1040 $cm^{-1}$, a broad peak of polyvanadate from about 750 to 970 $cm^{-1}$, and a small $V_2O_5$ peak at 998 $cm^{-1}$ (Fig. 2, curve c) (9). After reaction, the spectrum changed to the one shown in Fig. 2, curve d. The vanadyl peak disappeared. The original spectrum could be restored by heating the sample in oxygen. Unfortunately, no useful peaks were detected with X-ray diffraction with this sample.

To further investigate the relationship between the degree of reduction of vanadia and the selectivity in pentane oxidation, pentane pulse reaction studies were conducted over the $Al_2O_3$-supported samples (10). In these experiments, the catalysts were first pretreated in flowing oxygen at 500°C before pulses of 22% pentane in He were admitted. Over 23.4VAl, pulses of pentane at 300°C produced almost entirely CO and $CO_2$ and very little (<5%) selective products initially. The selectivity for maleic anhydride increased rapidly when the sample was reduced to an average oxidation state of vanadium of about 4.3, and reached a value of 56% when the average vanadium oxidation state was about four. In these experiments, the pentane conversion in each pulse was adjusted to be around 5% by adjusting the flow rate and the amount of catalyst used. The carbon balance in each pulse ranged from 85 to 95%. Thus, there was carbon deposit on the sample. The average vanadium oxidation state was estimated from the detected products, neglecting the carbon deposits. A similar trend was observed if the sample was reduced with CO before admitting the pentane pulse. The trend for sample 8.2VAl showed a similar gross feature. In the first pulse, only CO and $CO_2$ were produced. However, maleic anhydride was detected in increasing amounts in subsequent pulses, reaching 10% of the detected products when the average vanadium oxidation state was about four. The carbon balance for this sample was poorer, being only about 70% initially and rising to about 90% when the vanadium oxidation state was 4.

The trends observed in the pulse experiments were simi-

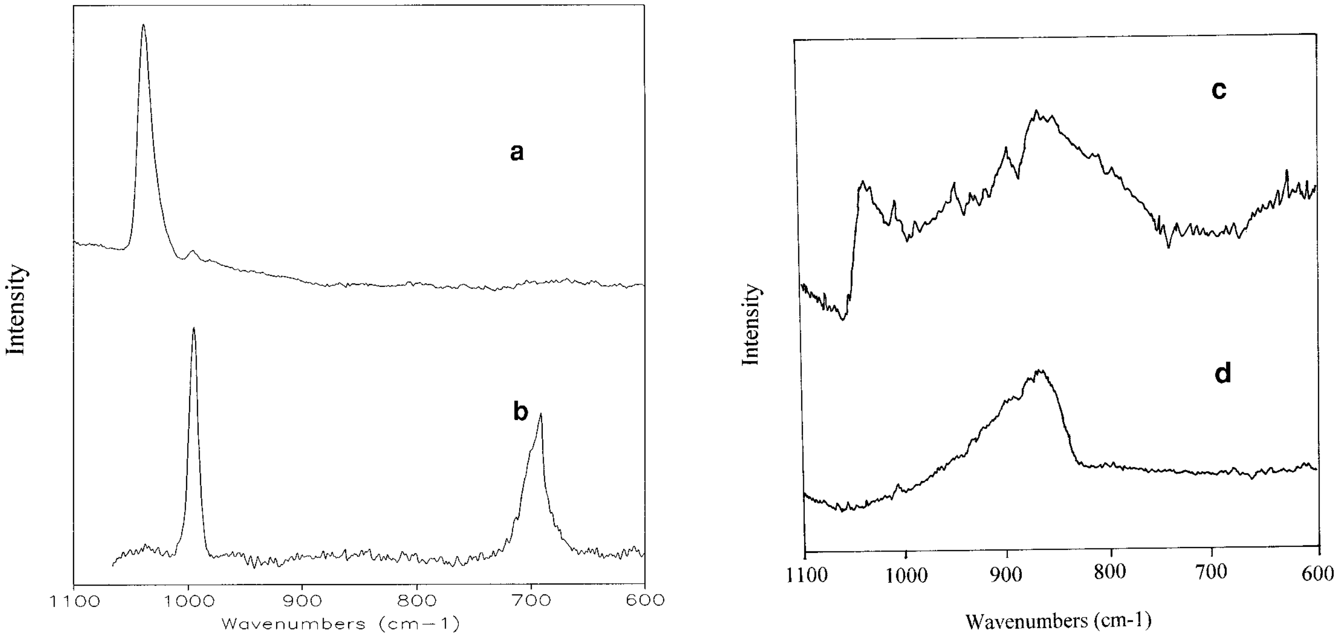

**FIG. 2.** Raman spectra of (a) 10VSi before reaction, (b) 10VSi after reaction and then reoxidized in air, (c) 23.4VAl before reaction, and (d) 23.4VAl after reaction.

lar to the steady state experiments in that the lower loading VAl sample was less selective for maleic anhydride production than the higher loading sample. They were also similar to butane oxidation: the selectivity for partial oxidation products increased with the extent of reduction of the sample.

The difference in the selectivity for partial oxidation products over the VSi samples of different loadings could be interpreted by the different species of vanadia on the silica support. At low loadings, vanadia exists as isolated vanadyl species. Such species have a limited number of oxygen atoms available to participate in an oxidation reaction. Therefore, these catalysts are selective for oxidative dehydrogenation, which requires only one oxygen atom to form alkenes and two to form diene. However, they are not selective for the formation of maleic anhydride from pentane because that reaction requires ten oxygen atoms. For this, polyvanadate units are more desirable. Thus, some maleic anhydride is observed on the high-loading VSi, which contained $V_2O_{5-x}$ crystallites under reaction conditions.

The Raman spectra of the VAl samples showed the presence of polyvanadates on both high- and low-loading samples (9). Thus, on the high-loading VAl sample, high selectivity for maleic anhydride could be obtained. On the low-loading sample, the lower selectivity for maleic anhydride might be due to the presence of exposed $Al_2O_3$. Results in Table 1 indicated that such exposed $Al_2O_3$ surface would degrade maleic anhydride to carbon oxides.

In addition to the nature of the vanadia species, the oxidation state of the vanadium ions is also important. We have shown previously that the differential heat of reduction of the $V_2O_5/\gamma\text{-}Al_2O_3$ increased with increasing degree of reduction (9). That is, removal of additional oxygen atoms from vanadia becomes increasingly difficult. Thus, the extent of reduction of vanadia under reaction conditions also determines the number of oxygen atoms available for oxidation, and consequently, the selectivity. The pentane pulse reaction data, which showed that maleic anhydride could only be produced with high selectivity when the average vanadium oxidation state is close to four is consistent with the observation that at steady state, the catalysts that produce maleic anhydride are reduced.

It is interesting to note that vanadium-substituted molybdophosphoric acid and vanadomolybdophosphate are quite selective in maleic anhydride formation in the oxidation of butane (11) and pentane (7, 8). Since each Keggin unit in these catalysts contains 12 bridge-connected reducible cations (V and Mo), there are potentially a large number of oxygen atoms available for hydrocarbon oxidation, which should facilitate the formation of oxygen-containing products over dehydrogenation products. This is in agreement with the earlier discussion.

## ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy, Basic Energy Sciences, and the Petroleum Research Fund administered by the American Chemical Society.

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Received January 19, 1995; revised September 6, 1995; accepted September 7, 1995