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# NOTE

# Role of Acid–Base Properties of $SiO_2$-Based Catalysts in the Selective Oxidation of Propane

The direct transformation of light alkanes into valuable products is one of the most challenging problems of catalytic chemistry since it could enable natural gas to be used as the feedstock for production of large-scale chemicals conventionally obtained from oil. Thus there is interest in producing propylene by direct oxidative dehydrogenation of propane (POD) on oxide catalysts. A large variety of unsupported and supported oxide catalysts has been claimed as being effective in the POD reaction (1–3). The V–Mg–O system has been extensively studied owing to its considerable catalytic activity, but we have recently documented that $V_2O_5/SiO_2$ catalysts possess a superior performance providing very high molar yield and productivity values (4). It has been pointed out that the rate as well as the reaction pathways and product distribution of the oxidative transformation of light alkanes depend on the acid–base properties of the solid catalysts (5). Generally, basicity promotes the dehydrogenation reaction, while acidity facilitates the formation of oxy-products (5). Notably, the POD reaction on V-containing catalysts (2, 4, 6), irrespective of their acid-base character, leads to the formation of propylene along with oxygenates and carbon oxides. However, no direct relationship between acid–base properties of the catalysts and product distribution have been provided. Considering the potential practical interest of the POD process, it is evident that the presence of acrolein and other aldehydes in the reaction stream (4) complicates the separation of the desired reaction product. Thus, the understanding of the factors controlling the formation of such oxygenated by-products could allow one to tune the chemical properties of the V-containing catalysts so as to improve their selectivity in the POD reaction. In order to contribute to this issue, we report here on the special influence of acid and base additives on the catalytic performance of a commercial silica sample, used as support of $V_2O_5/SiO_2$ catalysts (4), in the selective oxidation of propane.

A commercial “precipitated” $SiO_2$ (Si 4-5P, Akzo Product, BET surface area 400 $m^2\ g^{-1}$) has been used “as received” and modified by base (Na, K, Rb, Cs) and acid (P) additives. Base-doped $SiO_2$ samples were prepared by impregnation of the $SiO_2$ with aqueous solutions of the corresponding nitrate, while for the preparation of P-doped $SiO_2$ samples aqueous solutions of $H_3PO_4$ were employed. By properly dosing the amount of the precursor, a series of equimolar ($2.3$–$2.4 \times 10^{-4}$ mol/$g_{SiO_2}$) base-doped $SiO_2$ samples and two P/$SiO_2$ samples with P molar concentrations equal to $1 \times 10^{-5}$ and $1 \times 10^{-4}$ mol/$g_{SiO_2}$ were obtained. All samples were dried at 110°C for 10 h and subsequently calcined in air at 650°C for 12 h. The list of samples prepared, along with the values of surface area, chemical composition and dopant to silicon atomic ratio are given in Table 1.

Catalytic measurements in the selective oxidation of propane were carried out in a conventional flow quartz microreactor (i.d., 6 mm) connected on line with a GC (TCD, FID) system. The reagents and products have been analysed by a three-column system: (i) Porapak Q (length, 3 m; diameter, 1/8 in.) for the separation of $CO_2$, $C_2H_4$, $C_2H_6$, $C_3H_6$, and $C_3H_8$; (ii) Molecular Sieve (length, 3 m; diameter, 1/8 in.) for the separation of $N_2$, $O_2$, $CH_4$, and CO; and (iii) Carbowax 20M (length, 3.5 m; diameter, 1/8 in.) for the separation of oxygenates and $C_3H_4$. The activity of the above $SiO_2$ catalysts has been measured under the following experimental conditions: $T_R$, 450–575°C; $P_R$, 1 bar; $W_{cat}$, 0.25 g (particle size, 0.3–0.5 mm; diluted (1/1) with SiC). The molar composition of the reaction mixture was $C_3H_8:O_2:N_2:He = 2:1:1:8$, with a total flow rate of 100 $cm^3_{stp}\ min^{-1}$. The oxidation of propylene has been studied in the temperature range 500–550°C with the same amount of catalyst (0.25 g) and the reaction mixture $C_3H_6:O_2:N_2:He = 1:5:1:13$ flowing at the rate of 100 $cm^3_{stp}\ min^{-1}$. The blank tests with the empty reactor showed no $C_3H_8$ or $C_3H_6$ conversion under the studied conditions.

The acid–base properties of all the $SiO_2$ catalysts have been evaluated by $NH_3$ and $CO_2$–TPD tests. $NH_3$–TPD tests in the range 100–640°C were performed using 0.07–0.15 g of sample, He as carrier gas (25 $cm^3_{stp}\ min^{-1}$) and a heating rate ($\beta$) equal to 12°C $min^{-1}$. The catalyst sample was first treated *in situ* at 600°C for 1 h under $O_2$ flow and then cooled to 150°C. The sample was then saturated in a 5% $NH_3$/He mixture stream (25 $cm^3_{stp}\ min^{-1}$) for 1 h at 150°C and afterward the sample was flushed under the He carrier flow for 1 h at the same temperature. $NH_3$–TPD profiles were recorded using a quadrupole mass spectrometer (Thermolab, Fisons Instruments) connected on line with the reactor by a heated (180°C) inlet capillary system

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**TABLE 1**

**List of Samples**

| Sample code | Chemical composition | Surface area ($m^2 \cdot g^{-1}$) | Dopant/Si atomic ratio |
|---|---|---|---|
| Na-1 | 0.75% $Na_2O/SiO_2$ | 174 | 1/69 |
| K-1 | 1.1% $K_2O/SiO_2$ | 158 | 1/71 |
| Rb-1 | 2.2% $Rb_2O/SiO_2$ | 231 | 1/71 |
| Cs-1 | 3.4% $Cs_2O/SiO_2$ | 191 | 1/69 |
| Cs-2 | 5.3% $Cs_2O/SiO_2$ | 172 | 1/44 |
| P-1 | 0.067% $P_2O_5/SiO_2$ | 390 | 1/1588 |
| P-2 | 0.67% $P_2O_5/SiO_2$ | 352 | 1/158 |

(transit time $<0.5$ s). $CO_2$–TPD tests in the range 20–650°C were performed using 0.1 g of sample, He as carrier gas (30 $cm^3_{stp}$ $min^{-1}$) and $\beta = 10°C$ $min^{-1}$. The sample was first treated as previously described and then cooled to 450°C. The sample was then saturated in a $CO_2$ flow cooling from 450 to 50°C and further for 30 min at 50°C. Thereafter, the sample was flushed in the He carrier flow at the same temperature until stabilization of the baseline was reached. $CO_2$–TPD profiles were acquired using a TCD connected to a DP 700 Data Processor (Carlo Erba Instruments).

The catalytic properties of bare and modified $SiO_2$ samples in the range 500–575°C (reaction temperature $T_R$) are summarized in Table 2 in terms of $C_3H_8$ and $O_2$ conversion, specific reaction rate, and product distribution. All catalysts produce $CO_x$, olefins, and oxyproducts. The major product among olefins is $C_3H_6$, while among oxyproducts it is acrolein. From Table 2 it can be seen that in the adopted experimental conditions for all studied catalysts $C_3H_8$ conversion does not exceed 10%, while $O_2$ conversion was always less than 50%. $CO_2$ selectivity decreases generally with temperature. The selectivity to the products of selective oxidative transformation remains on the same level with temperature change even though in some cases a slight increase is observed.

On the bare $SiO_2$ the ratio of acrolein to propylene selectivity is about 0.5. The modification of the $SiO_2$ by basic additives has a remarkable effect on the product distribution. Indeed, the basic additives, particularly at 500°C,

**TABLE 2**

**Activity Data of Bare and Modified $SiO_2$ Catalysts in the Selective Oxidation of Propane**

| Catalyst | $T_R$ (°C) | $C_3H_8$ conversion (%) | $O_2$ conversion (%) | Rate ($\mu mol_{C_3H_8}$ $g^{-1}$ $s^{-1}$) | Selectivity (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | CO | $CO_2$ | $C_2H_4$ | $C_3H_6$ | $C_2H_4O$ | $C_2H_6CO$ | $C_3H_4O$ |
| $SiO_2$ | 500 | 0.90 | 3 | 0.49 | 20 | 20 | 5 | 37 | 2 | 1 | 15 |
| | 525 | 1.90 | 9 | 1.04 | 25 | 16 | 5 | 37 | 1 | 1 | 15 |
| | 550 | 3.10 | 15 | 1.69 | 28 | 14 | 7 | 33 | 1 | 1 | 17 |
| | 575 | 4.60 | 23 | 2.51 | 29 | 15 | 9 | 31 | 1 | 1 | 15 |
| Cs-1 | 500 | 1.70 | 8 | 0.93 | 28 | 19 | 2 | 16 | 4 | 2 | 20 |
| | 525 | 3.60 | 20 | 1.96 | 29 | 15 | 7 | 18 | 3 | 2 | 18 |
| | 550 | 5.70 | 30 | 3.11 | 34 | 11 | 9 | 34 | 3 | 1 | 15 |
| | 575 | 8.70 | 44 | 4.75 | 35 | 9 | 14 | 35 | 2 | 1 | 10 |
| Cs-2 | 500 | 1.50 | 8 | 0.82 | 23 | 16 | 2 | 14 | 4 | 3 | 24 |
| | 525 | 3.50 | 19 | 1.91 | 31 | 13 | 5 | 17 | 3 | 2 | 19 |
| | 550 | 5.70 | 30 | 3.11 | 34 | 13 | 8 | 19 | 2 | 1 | 15 |
| Rb-1 | 500 | 1.50 | 8 | 0.82 | 32 | 22 | 3 | 18 | 3 | 1 | 17 |
| | 525 | 2.20 | 12 | 1.20 | 30 | 16 | 6 | 24 | 2 | 1 | 18 |
| | 550 | 3.40 | 17 | 1.85 | 29 | 12 | 10 | 27 | 2 | 1 | 15 |
| | 575 | 6.20 | 26 | 3.38 | 30 | 8 | 15 | 32 | 1 | 1 | 10 |
| K-1 | 500 | 0.80 | 5 | 0.44 | 23 | 20 | 0 | 20 | 5 | 3 | 22 |
| | 550 | 4.00 | 22 | 2.18 | 30 | 12 | 8 | 24 | 3 | 1 | 17 |
| | 575 | 7.10 | 32 | 3.87 | 34 | 9 | 13 | 25 | 2 | 1 | 12 |
| Na-1 | 500 | 0.60 | 2 | 0.33 | 16 | 32 | 0 | 20 | 4 | 1 | 27 |
| | 550 | 2.60 | 12 | 1.42 | 31 | 16 | 9 | 25 | 3 | 1 | 16 |
| | 575 | 4.30 | 21 | 2.35 | 34 | 12 | 14 | 29 | 2 | 0 | 12 |
| P-1 | 525 | 1.70 | 8 | 0.93 | 23 | 22 | 4 | 38 | 3 | 0 | 11 |
| | 550 | 2.20 | 10 | 1.20 | 23 | 17 | 7 | 41 | 2 | 0 | 11 |
| | 575 | 2.80 | 14 | 1.53 | 21 | 14 | 9 | 44 | 1 | 0 | 11 |
| P-2 | 500 | 0.60 | 2 | 0.33 | 33 | 35 | 0 | 26 | 1 | 0 | 6 |
| | 525 | 0.90 | 3 | 0.49 | 32 | 25 | 7 | 29 | 0 | 0 | 6 |
| | 550 | 1.10 | 4 | 0.60 | 27 | 18 | 11 | 37 | 0 | 0 | 7 |

**TABLE 3**

**Acid–Base Properties of Bare and Modified Silica Catalysts**

| Catalyst | $NH_3$ uptake ($\mu$mol $g_{cat}^{-1}$) | $CO_2$ uptake ($\mu$mol $g_{cat}^{-1}$) |
|---|---|---|
| $SiO_2$ | 7.0 | 0.7 |
| Cs-1 | — | 13.5 |
| Cs-2 | — | 20.0 |
| Rb-1 | — | 13.5 |
| K-1 | — | 17.0 |
| Na-1 | — | 20.2 |
| P-1 | 14.7 | — |
| P-2 | 52.5 | — |

enhance more than twice the above acrolein/propylene ratio. For instance, at 500°C on the bare $SiO_2$, the selectivities to acrolein and propylene are 15 and 37%, respectively, whereas on the Cs-2 sample they are 24 and 14%, respectively. A similar trend has been obtained for all catalysts with basic additives (see Table 2).

In contrast, when $SiO_2$ is modified with acidic $P_2O_5$, the opposite trend occurs. The acrolein/propylene ration drops from 0.5 for bare silica to ca. 0.25 and 0.2 for P-1 and P-2 samples, respectively.

The acid–base properties of the bare and modified $SiO_2$ samples are presented in Table 3 in terms of $NH_3$ and/or $CO_2$ uptake. Such results show that the alkaline basic additives actually enhance the density of basic sites on the $SiO_2$ surface, while the acidic phosphorus additive increases the number of acid sites on the catalyst surface. In Fig. 1 the product distribution expressed as acrolein/propylene selectivity ratio is presented as a function of the surface basicity (A) and acidity (B) of the modified $SiO_2$ catalysts. It is evident that the increase of basicity implies a concomitant rise in the selectivity to acrolein, while acidic phosphorus additive shifts the product distribution toward the formation of propylene. The observed regularity between acid–base properties and product distribution is actually in contrast with previous studies which show that olefins, owing to their basic character, should be favorably formed on basic catalysts while oxygenates, being more acidic, should preferably be obtained on acidic catalytic systems (7, 8).

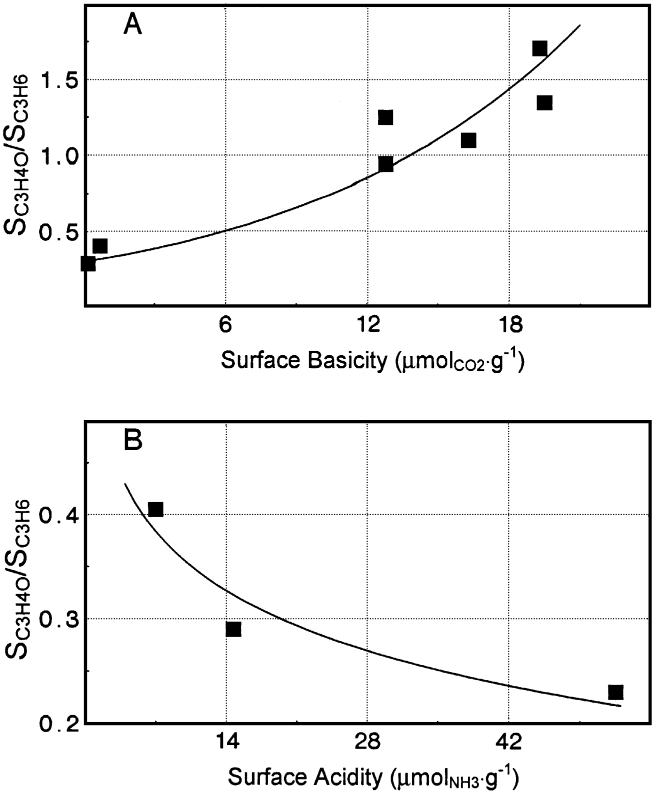

**FIG. 1.** Relationship between acrolein to propylene selectivity ratio ($S_{C_3H_4O}/S_{C_3H_6}$) and the concentration of (A) base and (B) acid sties of "modified" $SiO_2$ samples in the selective oxidation of propane at 500°C.

In order to rationalize the above results it can be inferred that acrolein is the product of the consecutive transformation of propylene. The occurrence of such a reaction pathway has been proved by performing a series of experiments of propylene oxidation on bare $SiO_2$ catalyst under operating conditions similar to those adopted in the selective oxidation of propane (similar temperature reaction range and similar $C_3H_6$ concentration in both the outlet stream of the POD reaction and the stream of propylene oxidation). The results, presented in Table 4, confirm the validity of the above hypothesis indicating that the oxidation of propylene on bare $SiO_2$ catalyst leads to the formation of acrolein and $CO_x$. Therefore, according to a general mechanism of hydrocarbon oxidation on oxide catalysts (9), it is likely that propylene activation occurs on the basic sites of the catalyst surface, resulting in the formation of allyl-anion species. On

**TABLE 4**

**Activity Data of Bare $SiO_2$ Catalyst in the Oxidation of Propylene**

| $T_R$ (°C) | $C_3H_6$ conversion (%) | $O_2$ conversion (%) | Rate ($\mu mol_{C_3H_6}$ $g^{-1}$ $s^{-1}$) | Selectivity (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | CO | $CO_2$ | $C_2H_4$ | $C_2H_4O$ | $C_3H_6O$ | $C_3H_4O$ | $C_3H_4$ |
| 500 | 17.0 | 9 | 2.5 | 42 | 31 | 3 | 3 | 1 | 18 | 3 |
| 525 | 30.0 | 18 | 4.5 | 43 | 31 | 3 | 3 | 0 | 18 | 3 |
| 550 | 49.0 | 34 | 7.3 | 46 | 28 | 4 | 2 | 0 | 18 | 2 |

the other hand, it has been shown previously that $SiO_2$ can create oxygen active species possessing electrophilic character (10) which can easily interact with electron-rich allyl-anion species giving rise to the formation of oxyproducts. On acid sites the activation of propylene could result in the stabilization of electron-deficient cationic species. The interaction of such carbocationic species with the above active oxygen species is rather hindered, and therefore on such an acid-promoted sample a slight $C_3H_6$ conversion rate should be expected.

The above mechanism of propylene activation on silica-based catalysts can also be proposed for the propane activation. In this latter case it is obvious that a higher surface basicity allows a higher overall reaction rate. We can then conclude that the acid-base character of the studied silica-based catalysts controls both the specific reaction rate and the product distribution. The basic promoter of the $SiO_2$ surface enhances the overall reaction rate, driving the reaction path toward the formation of acrolein, while the acid promoter causes a decrease in the reaction rate enabling preferentially the formation of propylene as the main product of the selective oxidation of propane.

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