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Activation of monolithic catalysts based on diatomaceous earth for sulfur dioxide oxidation

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Abstract

The formation of the active phases during the activation process of monolithic catalysts based on V_2O_5–K_2SO_4 supported on diatomaceous earth for SO_2 to SO_3 oxidation in flue gases, has been shown to be a crucial factor to achieve satisfactory catalytic performance. As the temperature is increased from room temperature to 470°C, SO_2 and SO_3 are taken up by the green catalyst and the precursors are transformed into the active species. The role of each component of the catalyst during the activation was analyzed by studying the behavior towards SO_2 adsorption of four materials, which contained: diatomaceous earth, diatomaceous earth + V, diatomaceous earth + K, and diatomaceous earth + V + K. The influence of the potassium sulfate accessibility in the green catalyst was studied by using two different preparation methods, which gave rise to differences in the catalysts SO_2 adsorption properties and catalytic performance. Furthermore, the influence of the activation atmosphere was studied using nitrogen, oxygen or a flue gas composition. It was shown that pyrosulfate species should be formed at temperatures below 400°C, to keep the vanadium in the active 5+ oxidation state.

Keywords: Monolith; Sulfur dioxide oxidation; $DeSO_x$; Catalyst activation

1. Introduction

The SO_2 contribution to the acid rain phenomena and its pernicious effects on ecosystems and human health have reinforced the development of more efficient cleaning technologies for the treatment of industrial gaseous emissions.

The catalytic oxidation of SO_2 traces to SO_3 seems to be one of the most feasible ways to carry out the desulfurization of flue gas from power stations. The catalyst commonly used in this SO_2 oxidation process corresponds to supported vanadium–alkali complex sulfates compounds which has been described as a molten–salt/gas $M_2S_2O_7/V_2O_5/SO_2/SO_3$ system, where M = Na, K and/or Cs.

Different research teams have been working in the characterization of the active species of these supported liquid phase (SLP) catalysts using various techniques, such as IR spectroscopy [1], ESR [2,3], Raman spectroscopy [4], potentiometry, cryoscopy, and spectrophotometry [5], calorimetry [6], density measurement and conductimetry [7] and NMR spectroscopy [8,9]. Although Fehrmann and co-workers have studied the phase changes in the temperature range 20–550°C for $Cs_2S_2O_7$–V_2O_5 [10] and $K_2S_2O_7$–V_2O_5 [11] systems, little is known about the activation of the active phase precursors, which would be expected to have influence on the performance of the final catalyst.

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In a previous work, the performance of this catalyst supported on a diatomaceous earth with monolithic geometry was tested for the treatment of flue gases from power stations; the results indicated that, at $T = 450^{\circ}C$, P = 120 kPa, GHSV (NTP) = 4900 h^{-1}, $[SO_2]$ = 1000 ppm, and $[O_2]$ = 5 vol%, SO_2 conversions higher than 80% might be achieved, if the previous activation of the catalyst is carried out properly [12].

The aim of the present work has been to study the different steps of the green catalyst activation process, which take place as the temperature is increased from room temperature to 470°C, the SO_2 and SO_3 are taken up by the green catalyst, and consequently the precursors are transformed into the active species.

2. Experimental

2.1. Catalysts preparation

A calcined diatomaceous earth (82 wt% SiO_2, 7.0 wt% Na_2O, 3.0 wt% Al_2O_3, 2.3 wt% Fe_2O_3, 1.2 wt% CaO, 0.7 wt% TiO_2, 0.3 wt% MgO, 0.3 wt% K_2O, 3.2 wt% other oxides) was used as support; potassium sulfate (99.94 wt% K_2SO_4, <0.7 wt% Cl^-, 4 wt% H_2SO_4, <0.2 wt% H_2O) and ammonium metavanadate (99 wt% NH_4VO_3, <0.2 wt% Cl^-, <0.05 wt% SO_4^{2-}, <0.3 wt% CO_3^{2-}) were used as potassium and vanadium precursors, respectively.

The catalysts were manufactured by extrusion of doughs prepared by two different procedures. In method A, the dough was prepared by kneading a mixture of diatomaceous earth and potassium sulfate powders, with an ammonium metavanadate aqueous suspension, to which oxalic acid was added to dissolve the salt. In method B, the potassium sulfate powder was added to vanadium salt aqueous solution, subsequently kneading the suspension with the diatomaceous earth powder to obtain the dough. In both procedures the obtained square-cell monoliths, after activation, had a cell density of 7.7 cells cm^{-2}, pitch of 0.36 cm, wall thickness of 0.09 cm, geometric surface area of 833 $m^2\,m^{-3}$, bulk density of 0.7 g cm^{-3} and a crushing strength of around 470 kg cm^{-2}. The V/K atomic ratio was 3.5, and the V_2O_5 content 7.4 wt%.

Furthermore, monoliths with similar geometry were prepared from some of the materials used for the catalysts manufacture. The compositions by weight of these samples are shown in Table 1.

Table 1
Composition by weight of the 6 cm length monolithic samples (g) before treatment

Sample	Diatomaceous earth	K_2SO_4	NH_4VO_3	Total
1	1.149	–	–	1.149
2	0.861	0.362	–	1.223
3	0.941	–	0.140	1.081
4	0.937	0.394	0.139	1.470

2.2. Activation and activity tests

Studies on the SO_2 adsorption capacity of the monolithic samples shown in Table 1 were carried out using a single channel of 6 cm length placed in a stainless-steel micro-reactor, operating with an inlet composition of: $[SO_2]$ = 700 ppm, $[O_2]$ = 3 vol% and [Ar] = balance, at a pressure of 107 kPa and GHSV (gas hourly space velocity, at normal conditions) of 3660 h^{-1}. The temperature was increased at a rate of ca. 5°C min^{-1} from room temperature to 470°C. The detection and quantification of SO_2 at the micro-reactor inlet and outlet was performed by mass spectrometry (Balzers Omnistar), using a channeltron detector.

The activation of the catalyst with different gas compositions and the catalytic activity measurements were carried out in a monolithic reactor working close to the isothermal axial profile, with gas mixtures containing $[SO_2]$ = 0 – 700 ppm, $[O_2]$ = 0 – 21 vol%, and $[N_2]$ = balance, at the following operation conditions: temperature = 25 – 470°C, pressure = 107 kPa and GHSV = 3200 h^{-1}; SO_2 contents were analyzed by Gas Chromatography (Varian 3400), using a photometric detector, and SO_3 measurements were carried out by volumetric analysis [13].

2.3. Characterization techniques

Laser Raman spectroscopy was used to study the samples surface compositions after use. The spectra were performed on the monolith walls at room temperature, with a Bruker RFS 100 spectrometer, exciting at 1046 nm with a Nd : YAG laser source. A germanium

diode cooled with liquid nitrogen was used for detection, with a resolution of 4 cm^{-1}. Laser power of 100–500 mW was used during the measurements. Before the measurements, the samples were irradiated for 2 h with a normal tungsten lamp, in order to reduce interference by the sample fluorescence.

The pore volumes were determined by use of mercury intrusion porosimetry (MIP) using CE Instruments Pascal 140/240 porosimeters. For these measurements, the values recommended by the IUPAC [14] of contact angle 141° and surface tension 484 m Nm^{-1} were used.

3. Results and discussion

3.1. Short-term SO_2/O_2 treatment

The SO_2 adsorption of the four materials shown in Table 1, as the temperature was increased at ca. 5°C min^{-1} up to 470°C and subsequently maintained at this latter temperature, is shown in Fig. 1 for the first 2 h in operation.

At low temperature (20–100°C) the four samples adsorbed large quantities of SO_2, which corresponds to physical SO_2 adsorption, and the adsorbed amount could be related to the pore volume of the samples, determined by mercury intrusion porosimetry: diatomaceous earth + NH_4VO_3 (0.35 ml g^{-1}) > diatomaceous earth (0.33 ml g^{-1}) > diatomaceous earth + K_2SO_4 (0.31 ml g^{-1}) > diatomaceous earth + K_2SO_4 + NH_4VO_3 (0.26 ml g^{-1}).

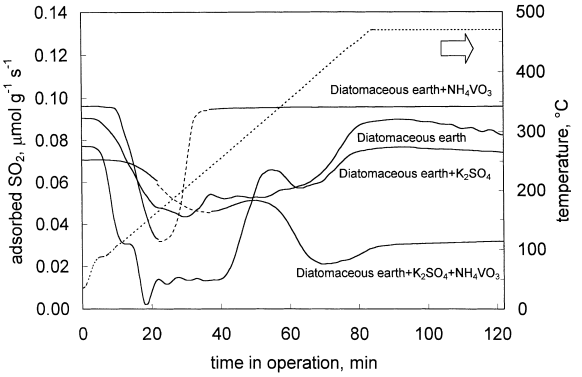

Fig. 1. Adsorbed SO_2 and operating temperature as a function of time in operation of the monolithic samples. [SO_2] = 700 ppm, [O_2] = 3 vol%, [Ar] = balance; GHSV = 3660 h^{-1}, P = 107 kPa.

3.1.1. Diatomaceous earth

After a decrease of SO_2 uptake above 100°C, at 350°C an increase in SO_2 consumption was observed, which can be assigned to the formation of sulfates from some of the oxides present in this material as impurities.

3.1.2. Diatomaceous earth + K_2SO_4

When potassium sulfate was added to the diatomaceous earth, a similar temperature/adsorption profile was observed up to 200°C, although the adsorption was lower than that observed with the diatomaceous. This decrease is probably due to a partial clogging of the diatomaceous earth inter- and intraparticulate pores by the potassium sulfate. A further increase of the temperature above 250°C led to higher adsorption, reaching a maximum at 330°C. This has been explained by the initiation of the $K_2S_2O_7$ formation by reaction of the K_2SO_4 with O_2 and SO_2, increasing the uptake of the latter; as K_2SO_4 and $K_2S_2O_7$ are solid at temperatures below 420°C, this phenomenon would be expected to occur only on the K_2SO_4 particles surface. The presence of any $KHSO_4$ impurities would increase this effect, by decreasing the melting point of the mixture, according to the phase diagram of the $K_2S_2O_7$–$KHSO_4$ [15].

3.1.3. Diatomaceous earth + NH_4VO_3

After adsorption at low temperature (assigned to physical adsorption), the sample containing diatomaceous earth and the vanadium lost NH_3 from 170° to 220°C. Above 220°C, a fairly constant SO_2 adsorption was observed, as vanadyl sulfate ($VOSO_4$) was starting to be formed.

The Raman spectrum of this sample (Fig. 2) shows not only the presence of characteristic V_2O_5 bands at 995, 706, 286, 200 and 145 cm^{-1}, but also the appearance of $VOSO_4$ (974 cm^{-1}). A similar behavior has been previously reported by Ivanenko et al. [16], who observed that the sulfation of V_2O_5 on silica led to the reduction of V(V) to V(IV) by the transformation of V_2O_5 to $VOSO_4$, at temperatures above 400°C.

3.1.4. Diatomaceous earth + K_2SO_4 + NH_4VO_3

The observations described above help to understand some steps of the activation pattern of the green catalyst: the SO_2 adsorption at low temperature

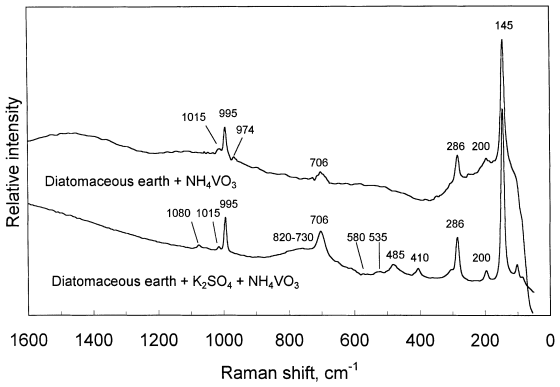

Fig. 2. Raman spectra of the vanadium containing samples after activation in $[SO_2] = 700$ ppm, $[O_2] = 3$ vol%, [Ar] = balance, for 2 h; GHSV = 3660 h^1; P = 107 kPa; $T = 25$–470°C (increasing rate ca. 5°C min^{-1}).

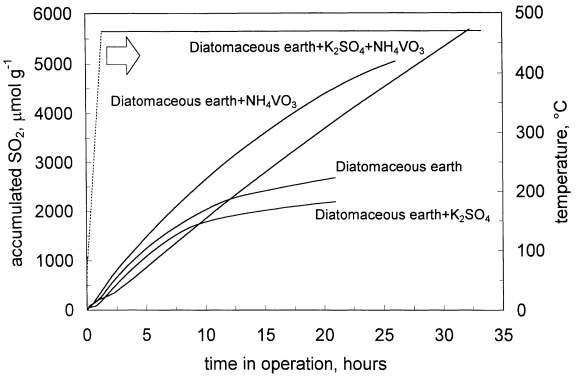

Fig. 3. Accumulated quantity of SO_2 and operating temperature as a function of time in operation of the monolithic samples. $[SO_2] = 700$ ppm, $[O_2] = 3$ vol%, [Ar] = balance; GHSV = 3660 h^{-1}; P = 107 kPa.

(25–100°C) due to physical adsorption, the exit of NH_3 from ammonium vanadate decomposition (170–220°C), and the formation of potassium pyrosulfate (250–370°C). However, the presence of the vanadium and potassium precursors simultaneously will give rise to alkali pyrosulfates which regenerate the active species V(V) by oxidation of V(III) and V(IV), that otherwise lead to deactivation of the catalyst [17]. The Raman spectrum of this sample (Fig. 2) shows characteristic S_2O_7 bands at 1080 and 730–820 cm^{-1} [18], besides other V_2O_5 characteristic bands (995, 706, 286, 200 and 145 cm^{-1}), and a band at 1015 cm^{-1} that has been generally assigned to surface vanadyl groups [19]. However, the $VOSO_4$ (974 cm^{-1}) is not observed. Above 330°C, the $K_2S_2O_7$–V_2O_5 eutectic would start to be formed [11,20] and fusion would take place, initiating the formation of the catalyst's liquid active phase. The SO_2 diffusion in the liquid phase would be less effective, and might be the cause for lower SO_2 adsorption observed in the 300–400°C range.

3.2. Long-term SO_2/O_2 treatment

Fig. 3 shows the accumulated SO_2 amounts as a function of time in operation when feeding with a gas mixture containing 700 ppm SO_2 and 3 vol% O_2, obtained with the four samples. The support (*diatomaceous earth*) tended to achieve a constant value after 20 h, indicating saturation of the sorption sites, ca. 0.192 g_{SO_2} $g_{solid}{}^{-1}$.

When adding K_2SO_4 (*diatomaceous earth* + *K_2SO_4*), also saturation was observed, although the total accumulated quantity was lower (ca. 0.140 g_{SO_2} $g_{solid}{}^{-1}$), indicating a pore clogging effect, as mentioned above.

The *diatomaceous earth + NH_4VO_3* sample accumulated larger quantities of SO_2, through the formation of vanadium sulfate. This would lead to a decrease in activity, due to the reduction of the catalyst active species, V(V), to lower undesired oxidation state. Additionally, some slight conversion of SO_2 to SO_3 has been observed.

In the case of the catalyst, *diatomaceous earth + K_2SO_4 + NH_4VO_3*, a continuous SO_2 accumulation/disappearance was observed, in which the SO_2 adsorption rate would be gradually substituted by the SO_2 to SO_3 conversion, as will be discussed later.

3.3. Influence of the potassium sulfate accessibility

The catalyst was prepared by two different methods, in which the only difference was the way in which potassium sulfate was added. In method A, the K_2SO_4 was added to the diatomaceous earth powder, while in method B the addition was made to the vanadium salt aqueous solution. The catalyst prepared by method B adsorbed lower quantities of SO_2 than that prepared by method A. The SO_2 conversions values for both

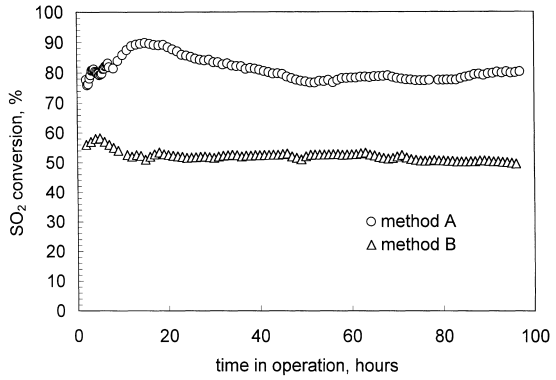

Fig. 4. SO_2 conversions at 470°C of monolithic catalysts prepared by two different methods as a function of time in operation; $[SO_2] = 700$ ppm, $[O_2] = 3$ vol%, $[N_2]$ = balance; GHSV = 3200 h^{-1}; P = 107 kPa.

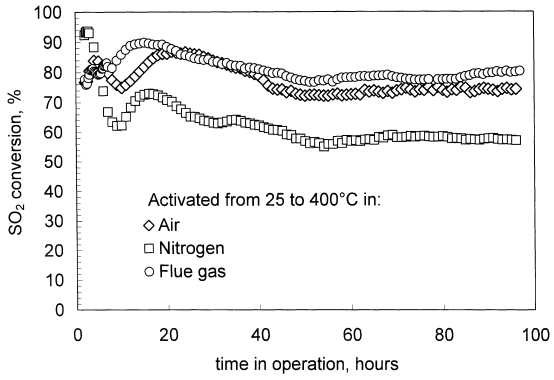

Fig. 5. SO_2 conversions at 470°C of the monolithic catalyst (method A) after activation in different atmospheres, as a function of time in operation. $[SO_2] = 700$ ppm, $[O_2] = 3$ vol%, $[N_2]$ = balance; GHSV = 3200 h^{-1}; P = 107 kPa.

catalysts shown in Fig. 4, clearly demonstrate that method A led to a much more active catalyst.

When the potassium sulfate particles are introduced into the vanadium salt solution — method B−, most of them might be covered by a vanadium salt layer that will limit their direct contact with SO_2 or O_2 during the activation process. With method A, however, the formation of the active phase is more favorable as the SO_2 has high accessibility to the potassium sulfate, which would be able to stabilize the V(V) as it is transformed to pyrosulfates at temperatures below 400°C. This was confirmed by Raman spectroscopy, as the catalyst prepared by method B showed much weaker V_2O_5 bands than the one prepared by method A (which showed a spectrum similar to the one presented in Fig. 2 as *Diatomaceous earth* + K_2SO_4 + NH_4VO_3).

The ratio between V_2O_5 and K_2SO_4 and the operation temperature have been pointed out as the two main parameters to be taken into account when designing catalysts for SO_2 to SO_3 oxidation [21]. The present results indicate that another important aspect might be the accessibility of the potassium sulfate, which allows an adequate pyrosulfate formation, leading to the V_2O_5 stabilization.

3.4. Influence of the activation atmosphere

The influence of the gas composition during the activation process on the catalyst activity was studied using the catalyst prepared by method A. In these experiments, the activation step was carried out in a flow of air, nitrogen, or an SO_2/O_2 mixture with a typical composition of a power plant flue gas ($[SO_2] = 700$ ppm, $[O_2] = 3$ vol%, $[N_2]$ = balance) increasing the temperature from 25 to 400°C, at a rate of ca. 5°C min^{-1}. When 400°C were achieved, the flue gas was fed into the reactor, and the temperature was further increased up to 470°C, in all cases. The SO_2 conversions are shown in Fig. 5 as a function of time in operation. In the three cases, total stabilization was reached only after ca. 50 h in operation. The highest conversion, 80%, was obtained when the activation step was carried out with the flue gas composition; 75% when air was used, and 57% if the activation process was carried out in nitrogen.

These results show that the key transformations that take place in the catalyst during the activation step are strongly affected by the presence of oxygen and SO_2. Activating in nitrogen would allow reduction of V(V) into undesired V(IV) and V(III) due to the presence of reducing agents, such as oxalic acid. If the activation is carried out in an oxidizing atmosphere (21 vol% O_2), the V(V) is stabilized; but when SO_2 is added at temperatures above 400°C, some may react with the V_2O_5 to form vanadyl sulfate with loss of catalytic activity. Therefore, the presence of SO_2/O_2 at temperatures below 400°C allowing the formation of the pyrosulfate species (320–370°C), which will give rise to the formation of the eutectic active composition [22], maintaining the stability of the V(V) state, is important.

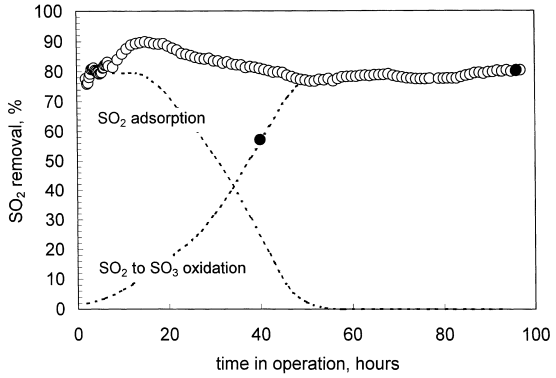

Fig. 6. Simultaneous SO_2 adsorption and SO_2 oxidation during the monolithic catalyst activation: (○) experimental SO_2 conversion, (●) experimental SO_3 formation, and (- - -) estimated SO_2 adsorption and SO_2 oxidation values. $[SO_2] = 700$ ppm, $[O_2] = 3$ vol%, $[N_2]$ = balance. $T = 470°C$; GHSV = 3200 h^{-1}; P = 107 kPa.

3.5. SO_2 adsorption vs. SO_2 oxidation

The long-term SO_2 disappearance can be interpreted in terms of an addition of both an SO_2 adsorption that gives rise to the formation of the active phases, and the initiation of the SO_2 to SO_3 oxidation by these newly generated species. In Fig. 6, the two processes are distinguished for catalyst A activated with a gas containing 700 ppm SO_2 and 3 vol% O_2. During the first 60 h, the monolith adsorbs SO_2 at a rate which decreases with the time in operation as the active phase is being formed. Meanwhile, the active phases start to transform SO_2 to SO_3 at an increasing rate, as was confirmed by determination of the SO_3 concentration at the reactor outlet, achieving the stable value that is observed on right side of the figure.

4. Conclusions

The results obtained in the activation studies with monolithic catalysts for SO_2 to SO_3 oxidation based on V_2O_5–K_2SO_4 supported on diatomaceous earth, indicate that the formation of the active phases is a crucial process in order to achieve satisfactory catalytic activities.

During this *activation process* it is necessary to form pyrosulfate species, which keep the vanadium in the active 5 + oxidation state, for which the following aspects should be taken into account:

- the activation should be carried out in oxidizing atmosphere and in the presence of SO_2.
- the formation of the pyrosulfate should take place as soon as possible, in order to limit the formation of vanadyl sulfate — V(IV) —, which will diminish the catalyst activity.
- the K_2SO_4 should be as accessible as possible to the SO_2 and O_2, at temperatures between 300° and 400°C.
- the presence of reducing agents such as CO or hydrocarbons during the activation process, would have a negative influence, as they will reduce the oxidation state of V(V).

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