Shielding Effect of Aluminium on Sulphur Dioxide Deactivation of Vanadium Oxide on Titania–Alumina DeNOx Catalysts

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Vanadium oxide supported on a TiO_2–Al_2O_3 mixed oxide prepared by gel-supported precipitation shows enhanced properties of resistance to deactivation by SO_2 during the selective removal of NO_x with ammonia in flue gases owing to the transfer of sulphate groups to Al sites.

There is considerable interest in the design of new improved catalysts for the selective removal of NO_x with ammonia (DeNOx) which can operate in the presence of SO_2.[1] In fact to comply with pending legislation on SO_2 and NO_x emissions, new technologies have been proposed for the removal of the two pollutants which presently require the use of SO_2-resistant DeNOx catalysts.[2] Vanadium oxide on TiO_2 is a well known catalytic system widely applied to the selective reduction of NO_x with ammonia.[3] However, in the presence of SO_2 the activity decreases rapidly owing mainly to fouling by ammonium hydrogensulphate deposition.[4–6] At temperatures higher than about 350 °C, owing to the vapour pressure of this compound, the rate of deactivation decreases, but the parallel rate of ammonia oxidation to nitrogen oxides that reduces the DeNOx efficiency becomes critical. High reaction temperatures, furthermore, make the application of the process to existing fire-boilers or power generating plants critical. Most recent industrial applications utilize mixed V_2O_5–WO_3 oxides on TiO_2 systems in order to reduce the rate of SO_2 to SO_3 oxidation but because of the lower activity of WO_3 these systems are active only at higher temperatures (>350 °C) with an increase in the parallel rate of ammonia combustion.[3]

In the analysis of the mechanism of SO_2 removal on CuO-Al_2O_3 sorbent–catalyst systems[7] we observed a surface transfer of sulphate groups from the copper-based sites to alumina-based sites. Consequently, we tried to apply the same concept in the design of a DeNOx catalyst based on vanadium oxide on a TiO_2–Al_2O_3 mixed oxide support in order to shield the vanadium DeNOx active sites from fouling by ammonium hydrogensulphate deposition through a surface transfer of sulphate groups to surface-available Al sites. This mechanism may prevent or limit the deactivation of the catalytic system.

The higher resistance of vanadium oxide on TiO_2 DeNOx catalysts towards poisoning by SO_2–SO_3 as compared to vanadium oxide on Al_2O_3 is known, but a direct comparison is not possible because (*i*) different vanadium oxide species are stabilized on the two supports, as shown also from the poorer performances of the latter system in DeNOx reactions, and (*ii*) these vanadium oxide species show different rates of SO_2 to SO_3 oxidation. In the TiO_2–Al_2O_3 system, in contrast, isolated Al sites are present together with the same vanadium oxide species interacting with titania surface sites present in the V–TiO_2 system, as confirmed from the similar DeNOx activity. It is thus possible to analyse better the specific effect connected with the presence of Al sites.

In order to have a homogeneous surface distribution of Ti and Al sites as well as to prepare samples with good mechanical properties and thermal stability, we adopted a method of gel-supported precipitation (GSP) for the preparation of the TiO_2–Al_2O_3 support.[8] This method, a variant of conventional sol–gel methods,[9] consists of dropping a homogeneous solution containing the starting Ti and Al compounds and organic additives into an ammoniacal solution in order to precipitate the mixed hydroxide. Owing to the formation of a gel during the precipitation step, segregation of distinct phases is prevented and a sufficiently homogeneous surface and bulk distribution of the Al sites in the TiO_2 matrix can be obtained.[8] The starting solution is obtained by dispersion of an aqueous $TiCl_4$ solution into an organic solvent immiscible with water until a stable emulsion is obtained. Aluminium is then introduced as a commercial colloidal $AlCl_3$ solution and then the aqueous phase is gelified by slowly adding a primary amine, extracting the Cl anion. The mixed hydroxide is already obtained in the form of microspheres after the precipitation stage; the sample, after filtration, is then washed, dried after extraction of the residual solvent and finally calcined at 500 °C with a temperature increase of 50 °C h^{-1}. Vanadium oxide (5% w/w as V_2O_5) is later deposited by an incipient wet impregnation method which provides a homogeneous distribution of V inside all the particles as verified by analysis of the concentration profile in the microparticle using microprobe analysis and scanning electron microscopy. In comparison to conventional sol–gel methods, this procedure allows nearly spherical samples to be obtained with good mechanical strength properties for application to mobile or fluidized bed reactors.

Reported in Fig. 1 is the comparison of the time-on-stream DeNOx behaviour of a series of vanadium oxide-based catalysts, during ageing tests in the presence of SO_2. In order to perform the tests on a laboratory-compatible time-scale, experiments were performed using a high SO_2 concentration and a low reaction temperature; in this way the rate of deactivation by fouling with ammonium hydrogensulphate deposition is maximized. The tests thus provide a comparison between the behaviour of vanadium oxide on a TiO_2–Al_2O_3 mixed oxide support and its behaviour on a TiO_2 system. At higher temperatures, where the rate of deactivation is reduced because of the vapour pressure of ammonium hydrogensulphate, the catalyst life-time is longer, but the same difference in the resistance to deactivation by ammonium hydrogensulphate deposition found in the low-temperature accelerated tests is expected.

The samples, all containing 5% of vanadium oxide, are supported on commercial TiO_2 (sample *a*), on a very high surface area TiO_2 (sample *b*), on a TiO_2 support prepared by gel-supported precipitation (sample *c*) and on a mixed TiO_2 Al_2O_3 support prepared by gel-supported precipitation and containing 20% by weight of alumina (sample *d*). In all samples, the TiO_2 was in the anatase crystalline form without the presence of a side TiO_2 rutile phase detectable by X-ray diffraction analysis. The catalytic tests were performed at 250 °C using an NH_3 to NO_x ratio of 1:1 and a GHSV (gas-hourly-space velocity) of 48000 h^{-1}. In order to have comparable data and to avoid mass-transfer limitations on the reaction rate, all catalysts were used in the form of powders with a grain size in the 0.125–0.250 mm range.

The threefold increase in the surface area of the TiO_2 (compare samples *a* and *b*) leads to an enhacement of the resistance to deactivation by SO_2 of the catalyst, owing to the increased surface area available for ammonium hydrogensulphate deposition, the presence of which was detected by FTIR characterization of the spent catalysts. However, it should be noted that the amount of vanadium oxide deposited on the TiO_2 corresponds to about 85 and 30% of the theoretical monolayer[10] for samples *a* and *b*, respectively. The relatively limited variation in the rate of deactivation thus indicates a specific fouling of vanadium sites by NH_4HSO_4 deposition and not a random distribution on the whole surface

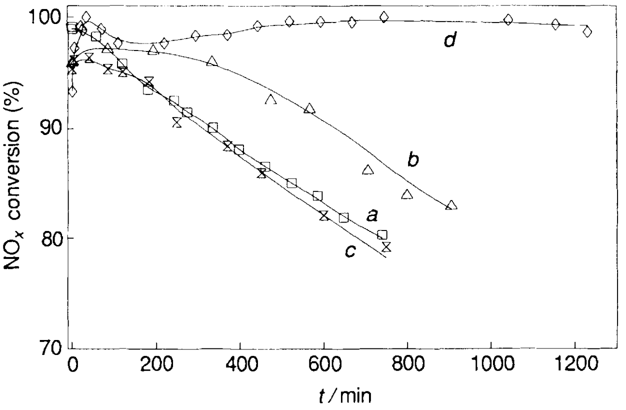

Fig. 1 Comparison of the time-on-stream DeNOx behaviour of a series of vanadium oxide (5% w/w as V_2O_5) catalysts on: *a*, TiO_2 (Degussa, 64 $m^2 g^{-1}$); *b*, TiO_2 (Tioxide, 173 $m^2 g^{-1}$); *c*, TiO_2 (prepared by GSP, 73 $m^2 g^{-1}$); *d* TiO_2 containing 20% by weight of Al_2O_3 (prepared by GSP, 139 $m^2 g^{-1}$). Feedstock composition: SO_2, 2000 ppm; NO, 800 ppm; NH_3, 800 ppm; space velocity, 48 000 h^{-1}; *T*, 250 °C.

area. Probably SO_2 is oxidized to SO_3 by vanadium sites and, before desorption, forms a stable sulphate on the surface, owing to the interaction with neighbouring $-OH$ and $-NH_4^+$ groups. In contrast, sample *d* with 20% alumina shows a relatively stable DeNOx catalytic behaviour and a very low deactivation rate, notwithstanding the fact that the surface area of the sample is lower than that of sample *b*.

This suggests the validity of the mechanism previously suggested of surface transfer of sulphate groups to Al sites. FTIR characterization, in fact, shows nearly comparable amounts of ammonium hydrogensulphate species as those found in samples *a* and *b* on the spent catalyst after comparable time-on-stream. The change in the deactivation rate is, therefore, not related to a change in the rate of SO_2 oxidation on vanadium sites, but is related more to a change in the surface location of the sulphate species. Furthermore, the comparison with sample *c* prepared in an analogous way, but without Al_2O_3, shows that the increased resistance to deactivation is not related to the method of preparation.

This suggests also that all the other methods known for reducing the rate of deactivation by SO_2 (such as use of tungsten oxide together with vanadium oxide, of higher reaction temperatures, or of thin films of the active component) may be effective, but the use of a mixed TiO_2–Al_2O_3 support instead of TiO_2 may further improve the catalyst life-time introducing an additional element of control, avoiding or limiting also the deposition of ammonium hydrogensulphate in the reactor outlet, in particular on the heat exchanger surface.

Finally, it should be noted that in sample *d* (containing Al_2O_3) a rapid increase is observed in the DeNOx behaviour after contact with the SO_2-containing flow. This effect is not observed in the absence of SO_2. Thus, the DeNOx activity of this sample is higher in the presence of SO_2 than without. It is well known[11] that sulphate groups on alumina increase the strength of Brønsted acid sites owing to inductive effects. The same effect is probably also present in the V–TiO_2–Al_2O_3 system, indicating the role of Brønsted sites in the DeNOx mechanism, in agreement with literature indications.[12] This is further evidence for the probable location of sulphate groups on the exposed surface Al sites of the TiO_2–Al_2O_3 mixed oxide support.

In conclusion, the data presented indicate that by suitable tuning and design of the surface properties of the support and, in particular, the introduction of elements that form more stable sulphate species, it is possible to enhance the resistance of DeNOx catalysts to deactivation by SO_2.

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