

On the importance of the phase distribution and acidity of VO_x-ZrO₂-SO₄-sepiolite catalysts for the NH₃-SCR process in relation to biomass fueled power plants

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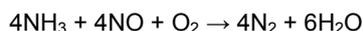
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Abstract

A series of V₂O₅-ZrO₂-SO₄²⁻-sepiolite mixtures were extruded, calcined and characterized. NH₃-SCR activity was related to the phase distribution of the agglomerant and active VO_x-ZrO₂-SO₄²⁻ phase, as well as the acidity of the composite material. Electrophoretic migration results showed that the addition of sepiolite to zirconia had effect on the quantity of zirconia present at the support's surface, both strongly decreasing the molar fraction of zirconia at the surface, and altering the electrophoretic properties of the mixtures. Addition of extra ammonia sulfate eliminate both effects, and thus facilitate the production of a sepiolite-based conformed catalyst based on VO_x-ZrO₂-SO₄²⁻, which has been shown to be more resistant to the industrially implemented V₂O₅-WO₃/TiO₂ catalyst.

Introduction

In recent years [1], the use of bio-fuels has attracted much attention in energy production since they are renewable energy sources which do not contribute to the greenhouse effect. Selective catalytic reduction (SCR) of NO_x with ammonia as reductant is the most efficient method to eliminate NO_x from flue gases produced in stationary sources (e.g. power plants) via the reaction



The traditional SCR catalyst suffers significant deactivation due to the presence of relative large amounts of potassium in the fly ash from bio-fuels. A possible solution to this problem is use of highly acidic supports [2], which would interact with potassium stronger than active metal species. Furthermore, this can be combined with the properties of sepiolite, providing physical strength and coverage for the active catalyst.

Experimental

Sulfated zirconia was prepared by impregnating Zr(OH)₄ (Melcat) with (NH₄)₂SO₄ (Panreac, > 99%) by the incipient wetness method. After digestion, the samples were dried at 150°C for 3 hours and then calcined at 500°C for 4 hours in air. Then a VOSO₄ solution was impregnated onto the sulphated zirconia, producing a slurry. Thereafter sepiolite, (Pansil 100, Tolsa S.A.) and water were added in the desired amounts to obtain a homogeneous paste with an adequate viscosity for extrusion by a syringe with a 2 mm orifice. The numeration "0/8" to "8/8" corresponds to weight fraction of sepiolite in V₂O₅-ZrO₂-SO₄²⁻, i.e. 0/8 being V₂O₅-ZrO₂-SO₄²⁻ and 4/8 corresponding to a 1:1 weight mixture of the catalyst with sepiolite.

Results and discussion

The X-ray diffractograms of the composites after extrusion and calcination at 500°C are depicted in Fig. 1. At 2θ = 28-32° the diffraction reflections from ZrO₂ is seen. Even though a small amount of monoclinic zirconia is observed, the predominating ZrO₂ phase is cubic, resembling much the tetragonal phase of ZrO₂.

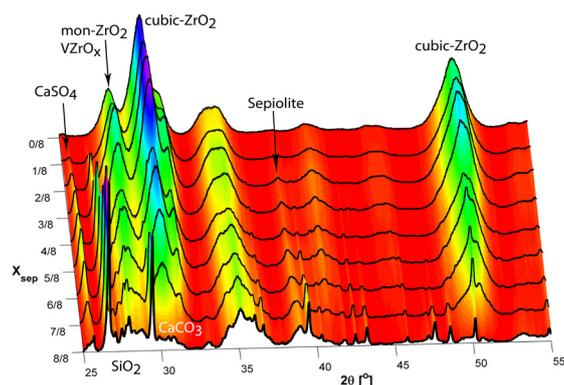


Figure 1 X-ray diffraction of $\text{VO}_x\text{-ZrO}_2\text{-SO}_4^{2-}$ /sepiolite composites after calcination at 500°C

At higher loadings of sepiolite, a Rietveld analysis suggests formation of a number of new phases, such as CaCO_3 and SiO_2 . At lower sepiolite concentrations CaSO_4 (sulfate from sulfated zirconia and Ca^{2+} from the sepiolite) and a small fraction of vanadium forming a solid solution with the zirconia is observed. The physical coverage of the zirconia phase by the sepiolite has also been confirmed by SEM analysis of the calcined catalysts (Fig. 2). Supported by zeta potential measurements, it is observed that at higher sepiolite loadings than 25% (2/8) the particles are covered by bundles of the sepiolite fiber material.

SCR activity tests of the catalysts have shown a larger decrease in activity with the decrease in $\text{V}_2\text{O}_5\text{-ZrO}_2\text{-SO}_4^{2-}$ loading than expected stoichiometrically. However, addition of extra $(\text{NH}_4)_2\text{SO}_4$ compensates for the formation of CaSO_4 and restores the surface acidity and activity.

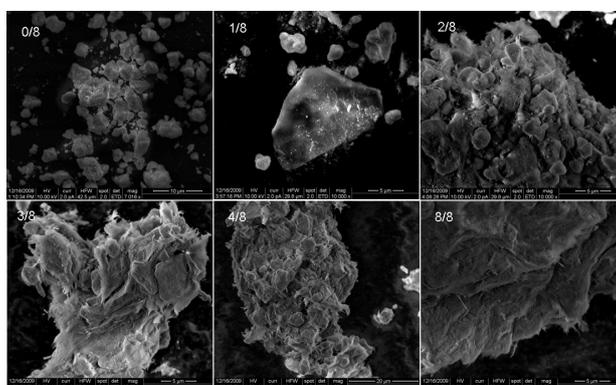


Figure 2: SEM micrograph of $\text{VO}_x\text{-ZrO}_2\text{-SO}_4^{2-}$ with increasing ratio of sepiolite

Conclusion

The preliminary extruded series of $\text{V}_2\text{O}_5\text{-ZrO}_2\text{-SO}_4^{2-}$ - Sepiolite hybrid catalysts were active in the SCR reaction. Although the coating sepiolite fibers has a “diluting” effect of the active phase of $\text{V}_2\text{O}_5\text{-ZrO}_2\text{-SO}_4^{2-}$, the corresponding enhancement in catalyst lifetime due to the covering sepiolite is an interesting candidate to a possible alkali resistant catalyst in biomass fired power plants.

References

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- [2] A.L. Kustov, S.B. Rasmussen, R. Fehrmann, R. Fehrmann, P. Simonsen, *Appl. Catal. B: Environ.*, **76**, 9–14 (2007)