REACTION KINETICS AND CATALYSIS LETTERS, Vol. 2, No. 3, 229–236 (1975)

MAGNESIUM FLUORIDE AS A SUPPORT FOR VANADIUM CATALYSTS

M. Wojciechowska, K. Nowinska, W. Kania and A. Nowacka

Institute of Chemistry, A. Mickiewicz University, Poznan, Poland

Received December 3, 1974

The applicability of MgF_2 as a support for vanadium catalysts of SO_2 oxidation has been studied. Catalysts were prepared by mixing the active components and the support as well as by impregnation of the latter. The mixed catalysts were found to have an enhanced activity, and the impregnated catalysts show a high mechanical strength.

Была изучена возможность применения Фторида магния в качестве носителя ванадиевого катализатора окисления двуокиси серы. Катализаторы были получены смешением каталитически активных компонентов с носителем, а также пропиткой носителя. Найдено, что смешанные катализаторы более активны а пропитанные катализаторы обладают повышенной механической устойчивостью.

Extensive research aimed at the improvement of catalysts for the oxidation of SO_2 has led to the evolution of preparations with very high activities. Their resistive capacity to mechanical damage, however, continues to pose a problem to the intensification of the output of sulfuric acid. Silica supports, though permitting to obtain highly active catalysts, fail to ensure the mechanical strength required in the highly efficient fluid process. Hence the search is continuing for a new support to meet the requirements of a fluid layer. Results obtained in this Laboratory on the properties of magnesium fluoride suggest it as a possible catalyst support. The high mechanical strength of the preparations obtained (6 on Mohs' scale) as well as their

thermal stability make it feasible to produce catalysts with the necessary properties. On the basis of earlier work /1/, we chose magnesium fluoride preparations with vanadium deposited on them in the form of various compounds by mixing with gels or by impregnation of pre-sintered grains. As promoter, potassium was used in the form of sulfate or carbonate. In order to permit a comparison of the activities of the catalysts obtained with industrial silica catalysts, we have assumed the amount of vanadium introduced to be approximately 10% V_2O_5. With regard to available results /2/ concerning the influence of the amount of K_2O on the activity of silica catalysts we have assumed that the optimum K_2O/V_2O_5 ratio is about 3.5.

EXPERIMENTAL

Magnesium fluoride for use as support for the vanadium catalysts studied was prepared as in Ref. /1/, by interacting hydrofluoric acid with a solution of magnesium sulfate. The white jelly thus obtained was rinsed with distilled and, subsequently, redistilled water to pH=4. The sample (labelled MF_7) was then divided into two portions, one of which was left in the state of gel, and the other dried at 105 °C and calcined at 550 °C for 5 hrs. The MgF_2 thus obtained (grain size 1-2 nm) was repeatedly subjected to impregnation with an aqueous solution of potassium sulfate and, subsequently, potassium vanadate or vanadyl sulfate. The composition of the solutions used is given in Table 1. The catalysts were then dried at 105 °C and activated at 550 °C for 5 hrs.

Another group of catalysts was obtained by mixing a wet MgF_2 gel with the respective compounds of vanadium and potassium /Table 1/. The products were then dried and subjected to activation as above.

Table 1

Preparation of vanadium catalysts supported on magnesium fluoride

Symbol	Type of catalyst	Components of solutions used in impregnation (per 100 g of support)						
		$VOSO_4$ (g)	KVO_3 (g)	V_2O_5 (g)	$H_2C_2O_4$ (g)	K_2SO_4 (g)	K_2CO_3 (g)	H_2O (g)
$MF_7VZ/1$	mixed	35	–	–	–	75	–	830
$MF_7VZ/2$	mixed	–	30	–	–	60	–	700
$MF_7VZ/3$	mixed	–	–	20	41	–	53	680
$MF_7V/1$	impregnated	23	–	–	–	18	–	150
$MF_7V/2$	impregnated	–	23	–	–	18	–	150

The V_2O_5 content of the catalysts was determined after Machovka /3/. The activity of the vanadium catalysts supported on magnesium fluoride was measured in sulfur dioxide oxidation in a typical flow device of the kind described by Malin et al /4/.

RESULTS AND DISCUSSION

The present paper is concerned with a study of the applicability of magnesium fluoride as a support for vanadium catalysts for the oxidation of SO_2. For this purpose, various potassium and vanadium compounds were deposited onto the support. Two groups of vanadium catalysts (mixed and impregnated) were obtained.

Table 2

Chemical analysis of the catalysts obtained by mixing the active components with MgF_2 gel

Symbol	Content		K_2O/V_2O_5
	V_2O_5 (%)	K_2O (%)	
$MF_7VZ/1$	9.9	17.8	3.5
$MF_7VZ/2$	9.6	18.3	3.7
$MF_7VZ/3$	9.5	16.6	3.4

Table 3

Chemical analysis of vanadium catalysts deposited on MgF_2 by impregnation

Symbol	Content subsequent to 1st impregnation		Content subsequent to 2nd impregnation		Content subsequent to 3rd impregnation		K_2O/V_2O_5 ratio after 3dr impregnation
	V_2O_5 (%)	K_2O (%)	V_2O_5 (%)	K_2O (%)	V_2O_5 (%)	K_2O (%)	
$MF_7V/1$	3.2	6.2	6.7	13.1	10.1	19.3	3.6
$MF_7V/2$	3.4	6.6	7.0	13.8	10.5	20.4	3.8

Their composition is given in Tables 2 and 3. The mole ratio of the active components differed but insignificantly from the theoretically proposed value, and amounted to:

$$3.8 \geqslant \frac{K_2O}{V_2O_5} \geqslant 3.4$$

Table 4

Activity of vanadium catalysts in terms of maximum degree of conversion in the reaction of SO_2 oxidation

Symbol	Temperature of maximum degree of conversion (°C)	Degree of conversion (%)
$MF_7VZ/1$	550	79.0
$MF_7VZ/2$	550	75.3
$MF_7VZ/3$	550	67.4
$MF_7V/1$	580	60.5
$MF_7V/2$	580	59.0

The percentage of V_2O_5 lay in the range:

$$10.5 \geqslant \%\, V_2O_5 \geqslant 9.5$$

The preparation of catalysts with the intended composition from a MgF_2 gel presented no difficulties, but the introduction of the active components by impregnation of the calcined support was difficult. It will be noted from the results of the chemical analyses in Table 3 that three impregnations are needed to introduce the appropriate amounts of active components. This difficultly is presumably a result of the small surface area of the support (of the order 30 m^3/g).

The catalysts were investigated in the reaction of SO_2 oxidation in the temperature range of 450–600 °C. The more active catalysts were those obtained by mixing vanadium and potassium salt solutions with a wet MgF_2 gel (Table 4, catalysts: $MF_7VZ/1$, /2, /3). The mixed catalysts give a maximum degree of conversion at 550 °C, whereas the impregnated catalysts show maximum conver-

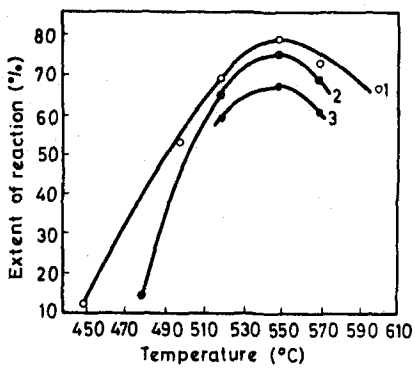

Fig. 1. Activity of vanadium catalysts deposited onto MgF_2 gel vs. the temperature of measurement in the reaction of SO_2 oxidation. 1 - $MF_7VZ/1$; 2 - $MF_7VZ/2$; 3 - $MF_7VZ/3$

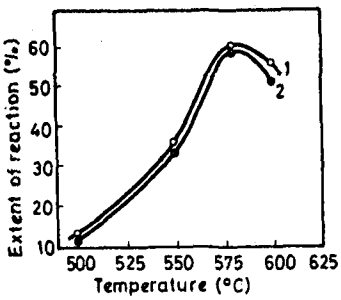

Fig. 2. Activity of vanadium catalysts, obtained by impregnation of MgF_2 vs. the temperature of measurement in the reaction of SO_2 oxidation. 1-$MF_7V/1$; 2-$MF_7V/2$

sion at 580 °C. The differences between the two groups are more apparent on the graphs showing the dependence of their catalytic activity on the temperature of measurement (Figs. 1 and 2). A particularly high activity was exhibited by the catalyst $MF_7VZ/1$ prepared by mixing a MgE_2 gel with solutions of $VOSO_4$ and K_2SO_4. Its activity expressed in per cent conversion amounted to 79% at 550 °C, a Polish catalyst tested under identical conditions yielded 96% conversion at 500 °C. The

catalysts impregnated with solutions of $VOSO_4$ and KVO_3 yield lower degrees of conversion (about 60%) but at the same time prove to be much more resistant mechanically than the catalysts deposited on a MgF_2 gel. Assessment of mechanical strength led to the following sequence:

$$\left.\begin{matrix} MF_7V/1 \\ MF_7V/2 \end{matrix}\right\rangle\!\!\rangle MF_7VZ/1 > MF_7VZ/3 > MF_7VZ/2$$

Generally, the catalysts obtained by impregnation have much more advantageous mechanical properties than those obtained by mixing with a gel. Presumably, the introduction of active components into a MgF_2 gel affects the MgF_2 structure adversely, thus causing a decrease in mechanical strength in comparison with that of the support MF_7.

A comparative study of activity and mechanical strength permits to divide the catalysts into two groups:

(1) Catalysts with a relatively high activity and low mechanical strength: $MF_7VZ/1$, $MF_7VZ/2$, $MF_7VZ/3$;

(2) Catalysts of lower activity but of considerable mechanical strength: $MF_7/1$, $MF_7V/2$.

Hence the work aimed at the improvement of the catalysts under investigation should continue in the direction of raising the mechanical strength of preparations obtained with the gel or of raising the activity of those obtained by impregnation. The factor decisive for the activity may well prove to be the $K_2O : V_2O_5$ ratio. The mechanical strength can be enhanced by thermal processing /5/; preliminary attempts in our Laboratory show that this should prove effective.

It should be noted that magnesium fluoride is a novel support still under testing, of which we have but limited knowledge, and the search to establish the optimum conditions with regard to preparative procedures, thermal processing, as well as the choice and amounts of active components still continues. It is our belief that further work on these interesting vanadium catalysts obtained on magnesium fluoride, will permit to develop a catalyst of very high quality.

REFERENCES

1. M. Wojciechowska, R. Fiedorow, W. Kuczynski: Acta Chim. Acad. Sci. Hung. (in press)
2. N. I. Buryak, Ye. I. Makarova: Vanadievye katalizatory dla kontaktnogo proizvodstva sernoy kisloty. Gos. Nauch. - Tekhn. Izd., Moscow 1963
3. P. P. Machovka: Zav. Lab., 23., 533 (1957)
4. K. M. Malin, N. Z. Arkin, G. K. Boreskov, M. G. Slinko: Tekhnologiya sernoy kisloty. Goskhimizdat, Moscow 1950
5. I. P. Muchlenov, Ye. I. Dobkina, Z. G. Filippova, N. P. Matveyeva, S. M. Kuznetsova: Zh. Prikl. Khim., 46., 1931 (1974)