UTILIZATION OF VANADIUM FROM USED INDUSTRIAL V_2O_5-TIO_2 CATALYST FOR THE PARTIAL OXIDATION OF O-XYLENE IN AN ULTRASONIC FIELD

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Abstract
Used vanadium oxide catalysts are still not completely exhausted and be utilized as regenerated catalysts. The present paper reports data on the extraction of vanadium from used industrial vanadium oxide catalysts for partial oxidation of o-xylene .The effect of various factors affecting the extraction (extragent concentration, temperature, duration, solid/liquid phase ratio, ultrasonic field) has been investigated and the optimum conditions of $H_2C_2O_4$ extraction of V_2O_5.A vanadium extraction degree of 82% has been achieved an extraction with $H_2C_2O_4$ in the presence of ultrasonic treatment.

Introduction
Some waste products from chemical industry such as used vanadium oxide catalysts for oxidation of o-xylene to phthalic anhydride are an important source of vanadium as raw material. The isolation of these products and their storage may be accompanied by vanadium coming in contact with the atmosphere and the hydrosphere, thus giving rise to certain ecological problems due to the toxicity of vanadium. Used industrial catalysts for o-xylene oxidation to phthalic anhydride are still regenerated and utilized.

Finding an optimum method for extraction of the active V_2O_5 component would facilitate the utilization of used catalysts as a potential source of fresh vanadium oxide catalysts and a lot of vanadium products.

The methods for extraction of the vanadium component include mainly chemical treatment with acids such as H_2SO_4, HCI, HNO_3, $H_2C_2O_4$ and citric acid [1-8], alkali hydroxides [9-11], alkaline melting with Na_2CO_3 (anhydrous) [12], ammonia [13], tetrachlormethane [14] and ion exchange methods [15]. Their disadvantages are the high temperature (above 100^o C) and the duration (2 to 4 h) of extraction.

The purpose of the present paper was to investigate the possibilities of utilizing the active V_2O_5 component of used industrial catalysts for obtaining fresh contact mass or other vanadium compounds. The method developed [16] for separating the used catalyst mass from the inert support in an ultrasonic field (US) was further perfectioned for simultaneous extraction of the vanadium component of used $V_2O_5 – TiO_2$ (a) catalyst with oxalic acid.

Experimental

The experiments on extraction of the active V_2O_5 component were performed with an F 04-25 industrial catalyst from BASF having been used for 3 years. Its composition is given in Table 1 [17].

Table 1 Chemical composition of the industrial catalyst F04-25 (BASF) [17]

Components	Composition, wt.%
V_2O_5	5-7
WO_3	0.06-0.1
Al_2O_3	0.1-0.3
P_2O_5	0.2-0.6
TiO_2(a)	92.0-96.0
$Me_2O^*_3$	0.001-0.005

*Me = Dy, Nd, Ho, Yb,

The catalyst consisted of an inert support (93% of the catalyst mass) in the form of porcelain spheres with a diameter of 0.5 mm and supported active mass [18-20]. At first we had to find an appropriate solvent with a view to achieving maximum extraction of the vanadium compounds from the used mass.

The effect of the following factors was studied:

- concentration of extractants;
- temperature of dissolution;
- process duration;
- liquid: solid phase ratio;
- effect of the duration of ultrasonic treatment.

Experiments without ultrasonic treatment proceeded with continuous intense stirring.

Some experiments with twofold oxalate extraction as well as a single oxalate extraction followed by a secondary water aqueous extraction were also performed. For that purpose, 200 cm^3 distilled water was added to the solid residue after the acid oxalate dissolution. The pulp obtained was allowed to stand for 12 h or was stirred for 3 h. This single acid extraction followed by water extraction decreased the amount of expensive oxalic acid used by one half.

Results and discussion

The experimental results concerning the dependences of V_2O_5 extraction from used catalyst samples upon temperature and molar V_2O_5: $H_2C_2O_4$ ratio are presented in Figs. 1-3.

The experimental curves indicate that temperature exercises no substantial effect on the extent to which vanadium passes into the solution and is extracted under the conditions of ultrasonic treatment. The increase of temperature during these experiments has only a weak effect of the degree of extraction. With samples subjected to ultrasonic treatment the increase of temperature has an essential effect on the extraction degree of V_2O_5 especially within the range of 60 –80^o C.

When the V_2O_5: $H_2C_2O_4$ molar ratio is varied (Figs. 1–3), the highest degree of V_2O_5 extraction in the absence of ultrasonic treatment is observed with a V_2O_5 : $H_2C_2O_4$ ratio of 1:5. The maximum V_2O_5 extraction in this case is 42.9 V_2O_5.

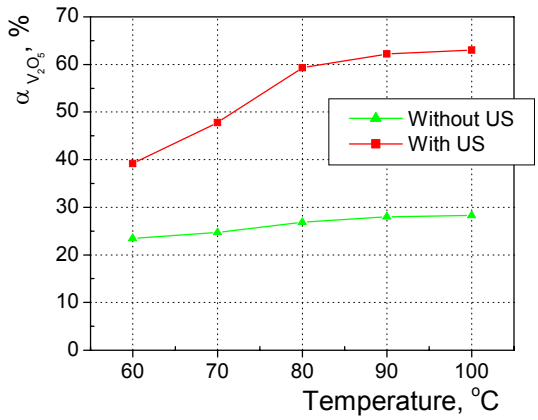

Fig.1 Dependence of the vanadium extraction (□$_{V2O5}$, %) on different temperatures, liquid/solid ratio V_2O_5 : $H_2C_2O_4$= 1: 3, □= 30 min

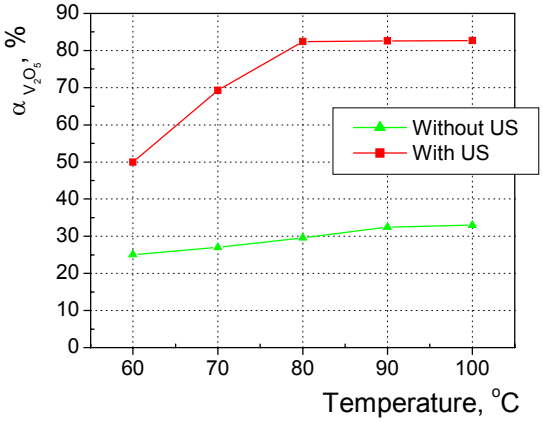

Fig.2 Dependence of the vanadium extraction (□$_{V2O5}$, %) on different temperatures, liquid/solid ratio V_2O_5 : $H_2C_2O_4$= 1: 4, □= 30 min

Samples subjected to ultrasonic treatment exhibit an essential increase of the degree of V_2O_5 extraction with rising V_2O_5: $H_2C_2O_4$ ratio from 1:3 to 1:4. In this case the maximum degree of extraction is α % = 82.6 V_2O_5. Further increase of the molar ratio up to 1:5 exercises no effect on the extraction degree.

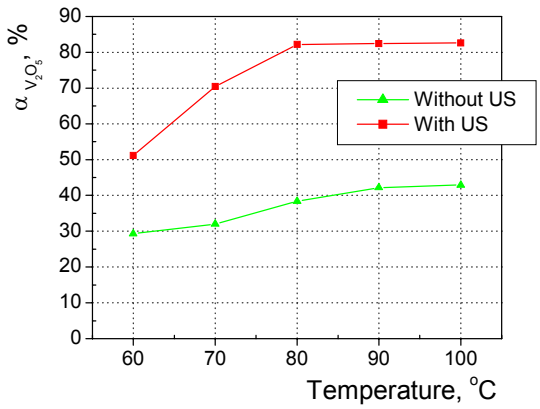

Fig.3 Dependence of the vanadium extraction (α_{V2O5}, %) on different temperatures, liquid/solid ratio V_2O_5 : $H_2C_2O_4$= 1: 5, □ = 30 min

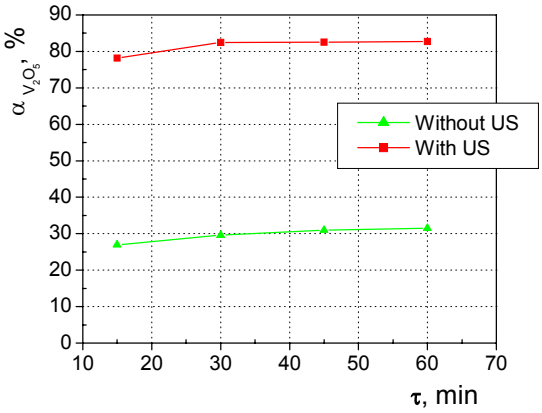

Fig.4 Kinetic curves of vanadium extraction (α_{V2O5}, %), solid/liquid ratio V2O5 : H2C2O4 = 1: 4, Temperature T = 80 °C

Studies on the effect of treatment duration (Fig. 4) have shown that in the absence of an ultrasonic treatment, a longer heating increases the extraction degree (from 27 to 31.5 % V_2O_5). Samples subjected to ultrasonic treatment reach a maximum extraction degree (above 82%) already during the first 30 min of treatment. With further increase of treatment duration, the extraction of V_2O_5 from the catalyst mass remains practically constant.

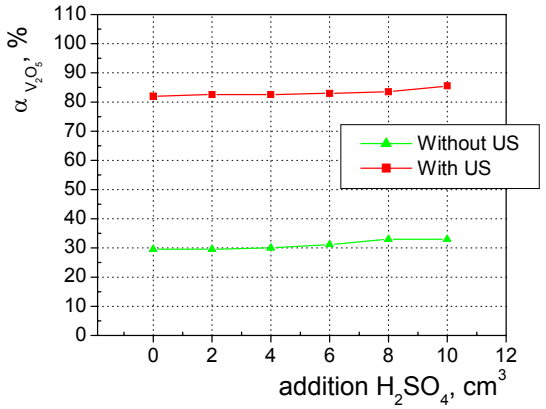

Fig.5 Dependence of the extent of vanadium extraction on the initial sulphuric acid concentration in the extraction solution, liquid/solid phase ratio V_2O_5:$H_2C_2O_4$ = 1 : 4, temperature T = 80 °C

The effect of an amount of 0 –10 cm^3 concentrated sulfuric acid in the reaction mixture has been studied with both kinds of catalyst samples (Fig. 5). Obviously, with rising additive amount, the extraction degree of V_2O_5 also increases with the two catalyst samples especially in the range of 8-10 cm^3 of added concentrated H_2SO_4. There a degree of extraction of 33 % V_2O_5 is attained without ultrasonic treatment, and 85 % V_2O_5 with this treatment.

Conclusions

On the basis of the experimental results obtained it may be concluded that:

1. Over the whole temperature range (60 –100^{o} C) extraction of the vanadium component from the catalyst mass of used V_2O_5 –TiO_2 (a) in the presence of ultrasonic treatment is more complete (82 %) than is the case without ultrasonic treatment (42.9%);
2. Addition of concentrated H_2SO_4 (8-10 cm^3) increases the degree of extraction with both catalyst samples (in presence and absence of ultrasonic treatment);
3. During ultrasonic treatment the increase of temperature affects essentially the degree of extraction at 60 – 100^{o} C;
4. An optimum extraction degree of vanadium from the catalyst mass is achieved with a V_2O_5: $H_2C_2O_4$ molar ratio of 1: 4 in the presence of ultrasonic treatment of 30 minutes**.**

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