

Site isolation based design of selective oxidation catalysts



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ABSTRACT

The paper summarizes results of using “dilution” approach for isolation of active sites in metal oxide catalysts. It is shown that the incorporation of catalytic inert elements, such as Mg, Al, Zr, Si, Hf, Ti and Nb, to the bulk of VSb and VMo oxides substantially increased their selectivity in partial oxidations of lower paraffins due to the structural isolation of V, Sb and Mo species. Herein the behavior of diluted oxides was dependent on the nature and amount of diluent material. The performance of diluted catalysts was further improved by tuning their surface properties. In particular, the selectivity of propane oxidative dehydrogenation to propylene was increased by making catalyst surface less acidic. On the contrary, the selectivity of propane ammoxidation to acrylonitrile was higher on more acidic surface built up by loading VSbAl oxide catalyst with tungsten. Phosphorus addition to the VMoNb oxide catalyst essentially improved selectivity of ethane oxidation to acetic acid also as a result of increasing surface acidity.

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1. Introduction

Site isolation is one of the important principles governing selective oxidation catalysis. It states that active sites must be spatially isolated from each other on a catalyst surface to achieve the selectivity. The postulate was first formulated and experimentally validated by Callahan and Grasselli 50 years ago [1]. They showed that the selectivity of propylene pulse conversion to acrolein was dependent on the number of oxygen ions in isolated groupings created by pre-reducing CuO catalyst. The maximum was observed at intermediate reduction levels which provided groupings containing two to five adjacent oxygens. Partially reduced catalyst, however, is hard to control and maintain under real catalytic reaction conditions when dioxygen is present in the feed. In this respect, structural methods of site isolation have advantage to potentially increase selectivity of a fully oxidized catalyst surface. This can be done by inserting catalytically active elements into the framework structure of low active materials such as zeolite, silicalite and ALPO [2,3]. This technique may produce highly dispersed isolated species which usually display higher selectivity than their aggregates. The drawback of thus prepared catalysts is low activity which often declines with reaction time. Active sites can be isolated also by preparing multicomponent phase in which active elements are separated from each other by less active elements or by vacancies. Classical example is selective α -Bi₂Mo₃O₁₂ phase, where Bi pairs are separated from each other by a cation vacancy [4]. This is not a case in the γ -Bi₂Mo₆ phase, which is

much less selective in partial oxidation of hydrocarbons than the α -phase. Another example is the (VO)₂P₂O₇ phase on the surface of which oxygen domains belonging to active vanadium doublets are isolated from other such domains by less active pyrophosphate groups. Each domain contains eight surface oxygens sufficient to oxidize an *n*-butane molecule to maleic anhydride, but insufficient to oxidize it to carbon oxides [5]. When active sites performing different functions cannot be separated in a single phase, alternative way is the preparation of multiphase catalyst where each phase contains a specific sort of sites. In this case, the phases must be in intimate proximity so that they can communicate with each other and thereby cooperate to provide catalyst proper functioning.

At SABIC Company we have employed the approach based on the incorporation of catalytically inert material to the catalyst body. Catalyst containing inert material has been called “diluted” catalyst to distinguish from the undiluted base catalyst. Both undiluted and diluted catalysts have been tested in the selective oxidation of C₁–C₃ paraffins.

2. Experimental

VSb-based oxide catalysts were prepared by thermal decomposition of the corresponding metal hydroxides co-precipitated with ammonium hydroxide from the mixed solution of ammonium metavanadate, antimony trichloride and, in the preparation of diluted catalysts, magnesium, aluminum or zirconyl nitrate. The precipitation was carried out at 80 °C and pH ranging from 8 to 10. The precipitate obtained was separated from the supernatant liquid by filtration when preparing Al- and Zr-diluted catalysts, and by evaporation for Mg-diluted catalyst. The reason that we chose evaporation rather than filtration for Mg-diluted catalyst was the

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uncontrolled loss of vanadium and in some cases magnesium during the filtration step in contrast to the Al- and Zr-diluted catalysts where the vanadium loss was negligible. The remaining cake or paste was dried at 120 °C for 6 h and then calcined in air at 650 °C for Al-diluted catalyst and at 800 °C for Mg- and Zr-diluted catalysts. Tungsten-loaded catalysts were prepared by impregnation of calcined diluted catalysts with aqueous solution of ammonium tungstate, followed by drying and calcination under the conditions used for the preparation of unloaded catalysts.

FeVSbAl oxide catalyst was prepared by mixing aluminum hydroxide precipitated from aqueous solution of aluminum nitrate with ammonium hydroxide, with the slurry obtained by mixing solutions of ammonium metavanadate, antimony chloride and iron nitrate. The resulting mixture was filtered to a cake, dried at 120 °C and calcined at 430 °C for 4 h and 650 °C for 4.5 h.

Nb-diluted VMO oxide catalyst was prepared by mixing solutions of ammonium metavanadate, niobium oxalate and ammonium paramolybdate under stirring at 90 °C. The resultant gel mixture was dried slowly to incipient wetness and then placed in an oven at 120 °C for 16 h. Dried solid was further calcined in air at 350 °C for 4 h.

BiAl oxide catalyst was prepared by mixing a solution of bismuth nitrate in aqueous nitric acid with a solution of aluminum nitrate and co-precipitating metal hydroxides with ammonium hydroxide. The mixed metal hydroxides were dried at 110 °C and calcined in air at 800 °C for 8 h.

Bulk compositions of catalysts were determined by ICP and XRD techniques. X-ray diffraction (XRD) spectra were recorded with a Philips X'Pert powder diffractometer, using $\text{CuK}\alpha$ radiation at 40 kV and 40 mA with continuous scan mode. Surface composition was studied by X-ray Photoelectron Spectroscopy (XPS) using Physical Electronics Quantum 2000 Scanning XPS equipment. The data were acquired using a probe beam of focused, monochromatic $\text{AlK}\alpha$ radiation. Raman spectra were obtained in a Bruker RFS 100 FT-spectrometer using NdYAG laser. Catalysts were studied at ambient conditions without pretreatment by accumulating 2000 scans with a 4 cm^{-1} resolution. Specific surface areas were measured by N_2 adsorption at 77 K using BET method. Surface acidity was studied by temperature-programmed desorption (TPD) of the preliminary adsorbed ammonia utilizing Hiden Mass Spectrometer (Model Hal 201) as a sensitive detector for the TPD system. Ammonia desorption was carried out in helium flowing with the rate 16 ml/min at the temperature rising from 150 to 900 °C with the rate of 25 °C/min.

Catalyst behavior in selective oxidation of C_1 – C_3 paraffins was evaluated in a conventional flow system with a fixed bed tubular reactor. A stainless steel reactor was coated with silica to suppress the non-catalytic oxidation of hydrocarbons. Oxidative coupling of methane was carried out at temperature 730 °C and atmospheric pressure in the $\frac{1}{2}$ " reactor which contained 8 cm^3 of catalyst (particle size 18–35 mesh) mixed with quartz chips. The feed of the $\text{CH}_4/\text{O}_2/\text{N}_2 = 30/20/50$ composition was flown at the rate 50 ml/min.

Ethane oxidation was performed in the $\frac{1}{2}$ " reactor charged with 3 g of catalyst (40–60 mesh) mixed with 0.6 g of silica of the same mesh. Reaction occurred at temperature 260 °C and pressure 14 bar. The feed consisted of 15% C_2H_6 , 18% O_2 and 67% N_2 . The flow rate was 30 ml/min.

Propane ammoxidation was conducted in the $\frac{1}{4}$ " reactor loaded with 5 ml mixture of quartz chips and 18–30 mesh catalyst the volume of which ranged from 0.2 to 2 ml. All catalysts were tested at atmospheric pressure and temperature 500 °C. The feed composition was standard consisting of 18% C_3H_8 , 8% NH_3 , 14% O_2 and the remainder He. The total flow rate was 50 ml/min. Contact time was varied by changing the amount of catalyst in the reactor.

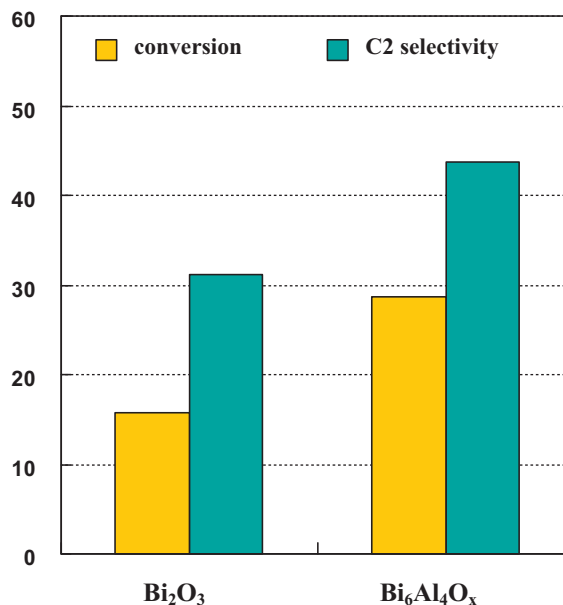


Fig. 1. Methane oxidative coupling on base and Al-diluted bismuth oxide catalysts at 730 °C and atmospheric pressure.

Oxidative dehydrogenation of propane was carried in the $\frac{1}{4}$ " reactor which contained catalyst granules of the 18–35 mesh mixed with quartz chips. A mixture of 10% C_3H_8 , 5% O_2 and 85% He was fed to the reactor at a total flow rate of 100 ml/min. Reaction temperature was 350 °C and pressure 1 bar. Contact time was varied by changing catalyst amount in the range from 0.5 to 5 cm^3 .

Reactants and products of all above reactions were analyzed on line by means of gas chromatography.

3. Results and discussion

The dilution approach has been tested on a number of oxidation catalysts which comprised monometallic (V_2O_5 , MoO_3 , Bi_2O_3) as well as multimetallic (VMO, VSb, FeVSb) oxides. The diluted catalysts were prepared by inserting catalytically inert and low active elements, such as Mg, Al, Zr, Si, Hf, Ti and Nb, to the bulk of listed oxide catalysts by means of co-precipitation technique. Most of diluted oxides turned out to be more selective catalysts than their undiluted analogs. This was the case for methane oxidative coupling to ethane and ethylene on Al-diluted bismuth oxide (Fig. 1), ethane oxidation to ethylene and acetic acid on Nb-diluted VMO oxide catalyst (Fig. 2), propane oxidative dehydrogenation to propylene on Al-diluted FeVSb oxide catalyst (Fig. 3) and propane ammoxidation to acrylonitrile on VSb oxides diluted with Zr, Al and Mg (Fig. 4).

The behavior of diluted catalysts was dependent on the nature of diluent material. In particular, the selectivity of propane ammoxidation to acrylonitrile on $\text{V}_1\text{Sb}_9\text{M}_6\text{O}_x$, where M was diluent, increased at isoconversion in the order $\text{VSbNb} < \text{VSb} < \text{VSbZr} < \text{VSbSi} < \text{VSbMg} < \text{VSbTi} < \text{VSbAl}$ indicating that aluminum was the most effective diluent for this series of catalysts. For a given diluent, the extent of dilution was a factor that affected catalyst behavior.

With increasing the amount of diluent, the selectivity of VSb oxides went through the maximum. The overall activity of some diluted catalysts was also higher than that of the undiluted ones because of the higher surface area. For instance, Fig. 1 shows that methane conversion on $\text{Bi}_6\text{Al}_4\text{O}_x$ was by 9% higher than that on Bi_2O_3 . This difference in activities can be explained by the difference in catalysts surface areas which were respectively 8.5 and 6.3

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