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Oxidative dehydrogenation of propane over niobia supported vanadium oxide catalysts

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Abstract

Oxidative dehydrogenation (ODH) of propane is examined over a series of catalysts, which include Nb_2O_5 supported monolayer V_2O_5 catalysts, bulk vanadia–niobia with different vanadium oxide loadings and prepared by four different methods, V_2O_5 and Nb_2O_5. The intrinsic activity (TOF) of the samples studied indicates that vanadium containing active sites are indispensable for catalytic oxidative dehydrogenation of propane. Variations in the chemical environment of the vanadium ion do not cause significant changes in activity per site and, hence, all samples show similar TOF when the rates are normalised to the concentration of V on the surface. Selectivity to propene on the other hand strongly depends on the nature of the catalyst because readsorption and interaction of propene with the acid sites leads to total oxidation. Optimization of the weak sorption of propene is, therefore, concluded to be the key factor for the design of selective oxidative dehydrogenation catalysts.

Keywords: Niobia supported vanadium oxide catalysts; Oxidative dehydrogenation of propane

1. Introduction

Oxidative dehydrogenation (ODH) of alkanes offers an energetically attractive route for the production of alkenes. Among the various catalysts proposed for this reaction, mixed oxide catalysts containing vanadium oxide are the most frequently studied. Much of this work has focused on mixed oxides of magnesia and vanadia [1–6]. Other vanadium oxide containing mixed oxides tested include alkali and alkaline earth orthovanadates [3,7], actinide orthovanadates [8], bulk vanadia–niobia [9], VAPO-5 [10] and vanadium oxide supported on amorphous $AlPO_4$ [11,12]. Most reports suggest that tetrahedrally coordinated vanadium favours high selectivity to alkenes, although opinions differ with respect to the exact nature of the active site. Orthovanadate [1–3], pyrovanadate [4,6] and isolated VO_4 tetrahedra [5,10], are all reported to be catalytically active and selective for oxidative dehydrogenation of propane to propene.

In this contribution, the ODH of propane is examined over a series of catalysts which include Nb_2O_5 supported monolayer V_2O_5 catalysts, bulk vanadia–niobia with different vanadium oxide loadings and prepared by four different methods, V_2O_5 and Nb_2O_5. The catalysts were selected to provide a series of oxides in

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which vanadium and niobium is present in different concentrations (and, hence, in different stoichiometries), and in different chemical environments. This is expected to enable conclusions to be made on the effect of the environment and the nature of the surface oxide complexes on the activity and selectivity for propane ODH.

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1. Bulk catalysts

A series of vanadia–niobia catalysts was prepared by methods described in detail elsewhere [13]. These methods included (i) adsorption of VO(acac)$_2$ onto niobia from a toluene solution, (ii) coprecipitation from a mixed oxalic acid solution of niobium and vanadium using aqueous ammonia, (iii) calcination of mixed oxalates prepared by evaporating solutions of vanadium and niobium oxalates to dryness (melt method) and (iv) impregnation of niobia with NH_4VO_3. These precursors were calcined for 5 h at 630°C. The Nb_2O_5 support was obtained from the Niobium Products Co., USA, and was calcined at 630°C for 15 h prior to use.

2.1.2. Monolayer catalysts

For the preparation of monolayer catalysts, vanadium triisopropoxide oxide (Alfa, 95%–98% purity) was deposited onto the Nb_2O_5 support (calcined at 450–500°C, BET area 55 m^2 g^{-1}) by incipient wetness impregnation. The solutions of the vanadia precursor in methanol were thoroughly mixed with the oxide support and dried at room temperature in a glove box for 16 h in a nitrogen atmosphere. The impregnated samples were subsequently heated to 120°C in flowing nitrogen. The final calcination was performed in O_2 (Linde, 99.99% pure) at 450°C. For comparison, a sample of V_2O_5 (Merck) was calcined at 450°C for 5 h in flowing air.

Details of the characterization techniques used are described elsewhere [13,14].

2.2. Catalyst testing

Catalytic testing was performed using a quartz tubular downflow reactor (I.D. 4 mm) operating at atmospheric pressure. A reactant mixture of 29 vol.-% propane, 9 vol.-% O_2 and 62 vol.-% He was used. The catalyst was used in the form of grains 0.3–0.6 mm in diameter and was diluted with quartz to give a bed length of approximately 40 mm. The amount of catalyst (70–600 mg) was chosen to allow for measurements in the required conversion range. The reactor outflow was analyzed using a HP 5880A GC equipped with a TCD detector and a molecular sieve 5A and a Heyesep Q column at 80°C.

The catalyst testing sequence involved heating the catalyst to 450°C at a rate of 15°C min^{-1} in the reactant stream with a flow of 140 ml STP min^{-1}. This temperature was maintained for 2 h to stabilize the catalyst. Measurements were then made at 425°C with varying space velocities over a period of approximately 10 h. For the determination of the reaction orders and activation energies, measurements were made between 385 and 435°C with a maximum propane conversion below 5%. Propene oxidation experiments were carried out using a feed of 20 vol.-% propene, 6 vol.-% O_2 and 74 vol.-% He flowing at 150 ml min^{-1}. Deactivation of the catalyst was not observed during the measurements. The reaction over quartz grains was observed to be negligible.

The turnover frequency, TOF (s^{-1}), was estimated for all the catalysts by normalising the rates to the surface V and Nb atoms. The number of surface vanadium and niobium atoms for the pure vanadia, pure niobia and bulk vanadia–niobia was estimated assuming the area occupied by $VO_{2.5}$ and $NbO_{2.5}$ to be 11 and 15 Å^2, respectively [15,16].

Table 1
Characterisation results and catalytic activity of vanadia–niobia catalysts

Preparation method	Conc. V (mol-%)		BET area (m^2 g^{-1})	XRD phase [a]	Rate [b] (μmol/m^2 s)	TOF (s^{-1})
	Bulk	Surf. [c]				
Coprecipitation	1.14	8.6	7.6	T	0.082	0.014
	1.64	10.3	7.3	T	0.093	0.015
	2.23	13.9	6.8	T	0.149	0.018
	3.15	15.2	7.4	T	0.180	0.020
	5.23	18.1	6.8	T	0.385	0.032
	7.12	20.9	8.2	T, tr B	0.510	0.029
	9.05	21.6	7.2	T, B	0.291	
Adsorption	2.15	12.6	19.9	T	0.227	
Impregnation	1.22	8.51	9.1	T	0.137	
Melt	1.01	2.6	38.6	T	0.038	

[a] T = T-Nb_2O_5, B = β-$(Nb-V)_2O_5$, tr = trace.

[c] Rate of propane consumption at 425°C.

[c] Estimated by LEIS.

3. Results and discussion

The physico-chemical characteristics of bulk vanadia–niobia catalysts are compiled in Table 1. For the coprecipitated catalysts, the surface concentration of vanadium increased in parallel to the bulk vanadium concentration. The surface concentration of vanadia for a particular bulk concentration in fresh catalysts, however, was also influenced by the preparation method. For example, the melt and coprecipitated catalysts with a bulk vanadium content of about 1 mol-% had surface vanadium concentrations of 2.6 and 8.6 mol-%, respectively. This is even more visible if the concentrations are normalised to BET surface areas of the catalysts. Thus, the preparation method influences drastically the surface concentration of vanadia.

The different preparation methods also led to different specific surface areas. The coprecipitated vanadia–niobia samples, for example, had a specific surface area of 7–10 m^2 g^{-1} while catalysts prepared by adsorption and impregnation had 19 m^2 g^{-1} and melt catalysts 39 m^2 g^{-1}.

Increasing concentration of vanadium (above 7 mol-%) led to a new vanadium containing phase β-$(Nb-V)_2O_5$, as seen by XRD measure-

Table 2
Characteristics of the monolayer catalysts

Sample	BET area (m^2/g^{-1})	V conc. (mol-%)	Rate [a] (μmol m^{-2} s^{-1})	TOF [b] (s^{-1})
Nb_2O_5	55	–	0.003	0.0003
0.5 V_2O_5/Nb_2O_5	53	0.5	0.029	0.028
2 V_2O_5/Nb_2O_5	48	2.0	0.180	0.039
4 V_2O_5/Nb_2O_5	46	4.0	0.360	0.038
6 V_2O_5/Nb_2O_5	43	6.0	0.451	0.029
8 V_2O_5/Nb_2O_5 [c]	40	8.0	0.336	
2% V_2O_5/Nb_2O_5 [d]	6.8	13.9 [e] (38.4 [f])	0.167	0.018

[a] Rate of propane consumption per unit surface area.

[b] Calculated assuming all vandium is on the surface (for Nb_2O_5 the number of Nb atoms on the surface).

[c] Vanadium loading greater than experimental monolayer loading.

[d] Bulk V_2O_5/Nb_2O_5 catalyst.

[e] Surface V concentration determined by XPS.

[f] Surface V concentration determined by LEIS.

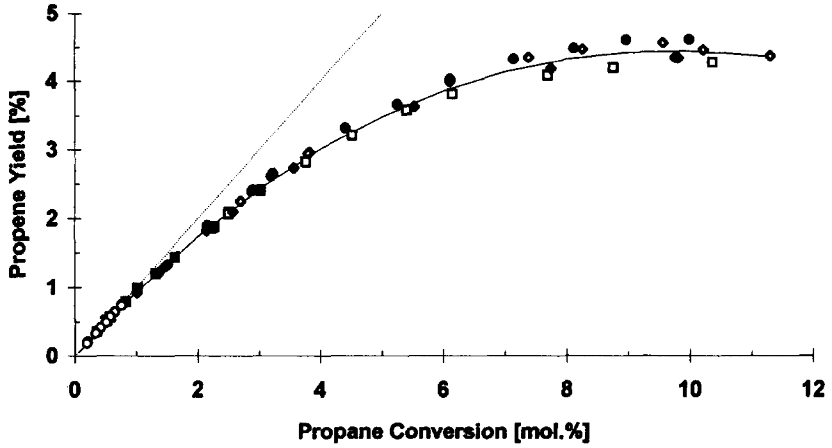

Fig. 1. Propene yield as a function of propane conversion at 425°C for bulk coprecipitated V_2O_5/Nb_2O_5 catalysts with 2.2% (●) and 7.12% V_2O_5 (◆), 2.15% V_2O_5/Nb_2O_5 prepared by melt method (○), 1.22% V_2O_5/Nb_2O_5 by impregnation method (◇) and 1.01% V_2O_5/Nb_2O_5 by adsorption method (□) (for details of catalysts see Table 1). All data points are at O_2 conversions < 95%. Dotted line indicates 100% selectivity.

ments. However, solid state ^{51}V MAS NMR measurements [17] showed that even in the case of samples containing low vanadia (up to 7 mol-%) vanadium exists in three different coordinations, i.e., in isolated tetrahedra, corner sharing dimeric tetrahedra and distorted octahedra. This allows to conclude that β-$(Nb-V)_2O_5$, which contains isolated V tetrahedra, is also present at much lower concentrations. The distorted octahedra and the dimeric vanadia species correspond to vanadium ions replacing niobium ions in niobia and free vanadia species, respectively. Thus, formation of the new phase occurs already at rather low concentrations. Niobia was present as an orthorhombic phase represented in literature as T-Nb_2O_5.

The physico-chemical characteristics of the monolayer catalysts are compiled in Table 2.

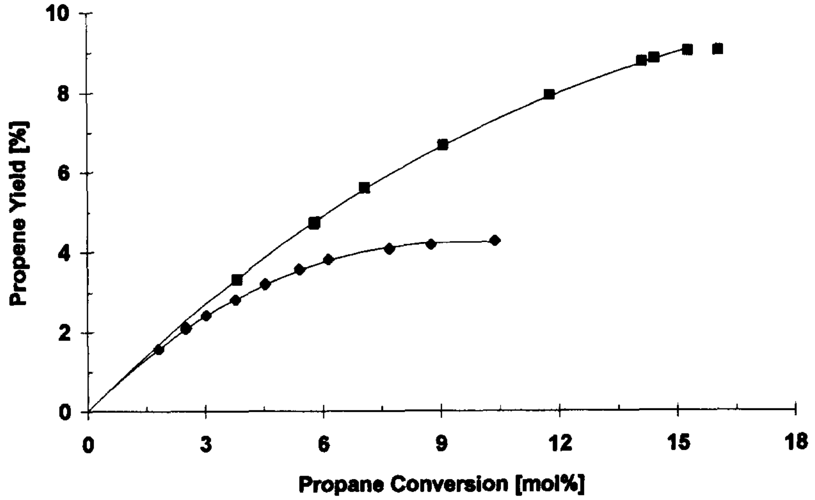

Fig. 2. Effect of temperature on the propene yield vs. propane conversion curves (■ 500°C, ◆ 425°C) for a 2% V_2O_5/Nb_2O_5 catalyst.

The results of the characterization of the monolayer vanadium oxide catalysts by Raman spectroscopy were previously reported in detail [14]. Raman bands due to crystalline V_2O_5 were not observed below a vanadia loading of 7%. Thus, the monolayer loading of surface vanadia was concluded to correspond to approximately 7%. The Raman spectra changed with the vanadium oxide coverage indicating the presence of isolated tetrahedral (low and high coverage) and polymeric (high coverage) surface vanadium oxide species [14]. Compound formation of a small part of the surface vanadium oxide species with the Nb_2O_5 support could not be excluded in these samples.

The most important data with respect to the catalytic properties of fresh samples are compiled in Fig. 1, Fig. 2, and Fig. 3 and in Tables 1 and 2. Fig. 1 shows the propene yields of the various vanadia–niobia bulk catalysts as a function of propane conversion. Note that for a given temperature all catalysts show an identical dependence of the propene yield upon the level of conversion. In contrast, the results obtained by Chaar et al. [2] do not indicate similar trends for V–Mg–O and V_2O_5 catalysts. Thus, despite the fact that each point in Fig. 1 corresponds to a different catalyst and that the data include catalysts that were prepared by different methods, with different vanadium loadings and containing different phases, the intrinsic surface chemistry seems to be identical. This strongly suggests that either propane ODH is insensitive to the surface structure of the catalyst or that under reaction conditions all the catalysts have nearly identical surface structures. The latter possibility would imply a quasi equilibrium between the catalyst phases and the existence of only one type of catalytically active site (or array of surface atoms).

Earlier studies on the ODH of propane have emphasized the importance of the V–O bonding on the catalytic activity. If the catalyst surface under reaction conditions corresponds to the surface characteristics at ambient temperature, this then is in contradiction to the model proposed here. The TOF for propane conversion for the various catalysts shown in Table 1 also supports the conclusion that rate of propane oxidation is insensitive to variations in the chemical environment of the active vanadium ion. Only minor variation in rate per surface vanadium site is observed. As outlined in the introduction, however, the concentration of these active sites and, hence, the catalytic activity per unit surface area of catalyst (see Table 1) varies with the chemical composition of the catalyst. This results in different propane conversions

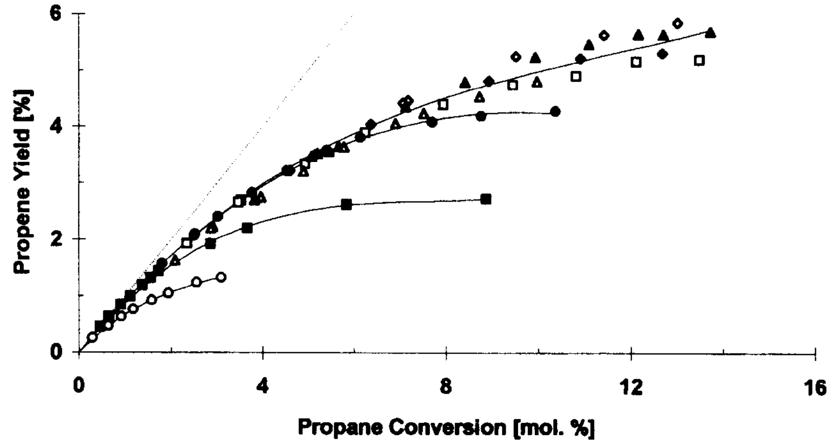

Fig. 3. Propene yield as a function of propane conversion at 425°C for Nb_2O_5 (○), V_2O_5 (■), bulk 2.2%V_2O_5/Nb_2O_5 (●) and Nb_2O_5 supported V_2O_5 with 0.5 (□), 2 (◆), 6 (▲) and 8%V_2O_5 (△). All data points are at O_2 conversions < 95%. Dotted line indicates 100% selectivity.

over the catalysts studied. It is this variation in conversion that causes the variations in selectivity.

In turning to the supported vanadium oxide catalysts, the catalytic activity per unit surface area was two orders of magnitude greater than that of the support alone (see Table 2). Vanadium is, therefore, concluded to be primarily responsible for the high catalytic activity. The rate of propane ODH per unit surface area increases first linearly with vanadia loading until 6% and then remains constant. This indicates that a monolayer loading of vanadia on niobia is reached at this point. Again the variation in the TOF's is small among the vanadium containing samples (between 0.028 and 0.039 s^{-1}). The rate of reaction seems to be determined only by the concentration of accessible vanadia and the amount of propane sorbed (for details see Refs. [2,9]). The active site for propane ODH in the vanadia/niobia system is, thus, concluded to contain a vanadium cation, which is shown by solid state NMR [17] and Raman spectral studies [14], to be present in a variety of stoichiometries at the surface.

Contact time variation experiments have previously shown that the main (consecutive) reaction reducing the selectivity is the sequential oxidation of propene. Thus, any means to reduce the interaction of propene with the catalyst surface inducing a lower concentration or residence time will be beneficial. Fig. 2 illustrates the improved selectivity for propene (for a given conversion) at a higher reaction temperature which is mainly attributed to the decreased surface coverage of propene at elevated temperatures. This increased selectivity for propene at higher temperatures has also been observed by Chaar et al. [2]. Similarly, the decreasing apparent energy of activation for propene oxidation among various catalysts, i.e., $6V_2O_5/Nb_2O_5$ (monolayer catalyst) 157 kJ/mol, 1.5% V_2O_5/Nb_2O_5 (bulk catalyst) 128 kJ/mol, V_2O_5 118 kJ/mol and the parallel decrease in selectivity to propene (see Fig. 3) indicates a parallel variation in the heat of adsorption of propene and the selectivity. It is speculated that the high apparent energy of activation is primarily a sign of the lower heat of adsorption and, hence, of the lower acidity of the material. Most likely the preparation of the monolayer catalysts reduces more effectively the concentration of strong Lewis acid sites than any of the other methods chosen. This explanation is in line with the suggestions of Kung and coworkers [1,2,8] that it is the basic nature of the MgO support that reduces the strength in the propene sorption and enhance the selectivity in V–Mg–O catalysts.

4. Conclusions

The intrinsic activity (TOF) of the samples studied indicates that vanadium containing active sites are indispensable for catalytic oxidative dehydrogenation of propane. All samples show similar TOF when the rates are normalised to the concentration of V on the surface. Either the variations in the chemical environment of the vanadium ion does not cause significant changes in activity per site and, therefore, the reaction is insensitive to these changes or under reaction conditions all catalysts form in equilibrium rather similar surface structure. Selectivity to propene on the other hand strongly depends on the nature of the catalyst because readsorption and interaction of propene with the acid sites leads to total oxidation. Optimization of the weak sorption of propene is, therefore, concluded to be the key factor for the design of selective oxidative dehydrogenation catalysts.

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