Oxydehydrogenation of propane over Mg–V–Sb-oxide catalysts. I. Reaction network

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Magnesium vanadates have been shown by various groups to be active oxydehydrogenation catalysts for the conversion of light paraffins to the corresponding olefins. The olefins produced have significant commercial value in petroleum and petrochemical industry. Recently, we reported that doping of the magnesium vanadates with antimony, antimony–phosphorus, or boron, produces catalysts with significantly better selectivities to olefins than those of the parent undoped catalysts. Among these, the composition $Mg_4V_2SbO_x$ was selected for further study of propane oxydehydrogenation and its reaction network. At 500°C and atmospheric pressure, the selectivity to propylene decreases monotonically from 75% to 5% as propane conversion is increased from 2% to 68%. An analysis of the reaction network reveals, that propylene is the only useful first formed product, that CO_x is produced largely by sequential oxidation of the in situ formed propylene, but also to a lesser extent direct from propane by a deep oxidation route. The presence of two parallel pathways for CO_x formation is of interest, as it suggests that partial and deep oxidations may occur at different surface sites or involve different forms of reactive oxygens. Both of these might be amenable to electronic modification by substitution or doping to achieve higher propylene selectivities and yields at higher propane conversions, or their catalytic behavior might be advantageously alterable through site isolation of the paraffin activation centers.

Keywords: oxydehydrogenation; propane; propylene; Mg–V–Sb-oxide catalyst; reaction network

1. Introduction

Oxidative upgrading of light paraffins to the corresponding olefins, diolefins and/or oxygenated products is of industrial interest [1]. Olefins produced in this manner can be used as alkylation or etherification feedstocks to enhance the octane number pool of refinery streams, while oxygenates can be added directly to reformulated gasoline to increase both its oxygen content and octane number.

Binary Mg–V-oxide systems [2,3] have been shown to catalyze oxidative dehydrogenation of propane and butane with good activity but poor selectivity. In a recent study [4], we have demonstrated that the selectivity to useful products, as well as the redox properties of the Mg–V-oxide base can advantageously be modified by the addition of certain doping elements. The survey showed that the addition of antimony, antimony plus phosphorus, or boron resulted in catalysts with significantly improved activity and selectivity for oxydehydrogenation of *n*-butane. One of the most improved catalyst compositions was $Mg_4V_2Sb_2O_x$, giving a selectivity to butenes of 85% at 3% butane conversion, at 500°C and atmospheric pressure.

In the current study we investigated the oxydehydrogenation of propane to assess the catalytic behavior of $Mg_4V_2Sb_2O_x$ and its reaction network.

2. Experimental

The synthesis and characterization of $Mg_4V_2Sb_2O_x$, as well as, the methodology of catalyst evaluation have been described previously [4]. In the current study, aimed at determining the reaction network of propane oxidation over this catalyst, the oxygen mole fraction of the feed in all experiments was kept at 25 mol%, while the propane mole fractions were varied to give oxygen : propane ratios of 1 : 1, 2.5 : 1, and 6 : 1. In one experiment, propylene was fed in place of propane at an oxygen : propylene ratio of 1 : 1, to assess its reaction pathway. In all cases, the feed was diluted with helium to help moderate the exothermicity of the reaction. Measurements were made at flow rates between 21 and 270 sccm with 2 g of catalyst, to yield a range of space velocities (WHSV) of 0.3 to 11 h^{-1} based on propane in the feed. Reactor feed and product compositions were determined by on-line gas chromatography. All results are presented on a no-loss-of-carbon basis. Typical carbon and hydrogen closures were 97% or better, oxygen closures 95% or better.

The background homogeneous phase reactivity of propane and propylene with oxygen, measured in a reactor packed with quartz chips, was insignificant even under the most severe conditions studied. After a 6 h

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line-out period, the activity and selectivity of the $Mg_4V_2Sb_2O_x$ catalyst remained constant through the duration of these experiments, giving an indication of its good stability under reaction conditions.

3. Results and discussion

The only products detected in propane oxidation over $Mg_4V_2Sb_2O_x$ at 500°C were propylene, CO, and CO_2. The selectivity to propylene decreases monotonically with propane conversion and is essentially insensitive to the oxygen-to-propylene ratio in the feed. A six-fold excess of oxygen in the feed produces only a modest reduction in selectivity over the entire range of propane conversions (fig. 1). This behavior is common for oxidation catalysts and implies that the lattice oxygen of the catalyst is primarily involved via a redox process in the oxydehydrogenation process of this catalyst. An independent set of pulse experiments, using no gaseous oxygen in the feed, confirmed this conclusion, since the $Mg_4V_2Sb_2O_x$ catalyst produced under these conditions also propylene and CO_x.

The monotonic decline observed in the partial oxidation selectivity is common in hydrocarbon oxidation, typically resulting from the sequential oxidation of a first formed partial oxidation product (e.g., propylene, acrolein, etc.) to CO_x (fig. 2). However, similar behavior would be observed if propane were oxidized in parallel to propylene and CO_x, as long as the deep oxidation rate were higher-order in oxygen than the partial oxidation rate. Discrimination between these possibilities is important in order to understand, and hopefully rectify, the loss of olefin selectivity at high propane conversion.

The reaction network can be determined by a simple analysis of selectivity–conversion plots [5]. According to this method, primary products of a given reaction can be discriminated from higher-order products by evaluation of the zero-conversion intercept of their selectivity. Primary products have non-zero intercepts, secondary and higher-order products have zero intercepts. This analysis is general and is independent of the reaction kinetics.

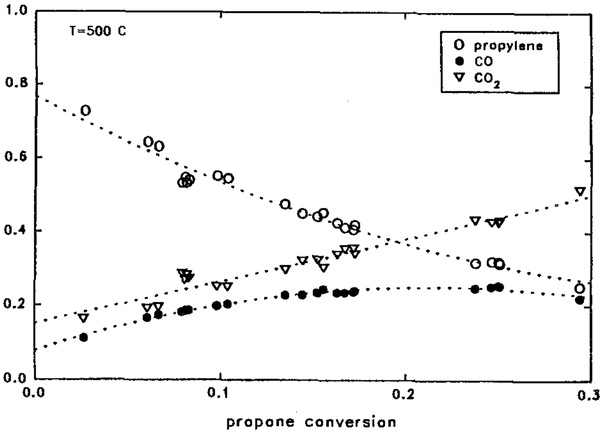

Fig. 2. Propylene, CO, and CO_2 selectivity profiles in propane oxidation over $Mg_4V_2Sb_2O_x$. $C_3 : O_2 = 1 : 1$.

Propylene, CO, and CO_2 selectivities measured at 500°C with a 1 : 1 oxygen : propane feed reveal that the propylene and CO_2 selectivities are not nil at zero conversion, indicating that both compounds are primary products of propane oxidation (fig. 2). Determination of the intercept of the CO selectivity is not straightforward, as extrapolation through the origin or to a non-zero intercept are both plausible. However, the propylene and CO_2 selectivities at zero propane conversion do not sum to unity, and this suggests that the CO selectivity should be extrapolated to a non-zero intercept, as shown in fig. 2. For this reason, we conclude that CO and CO_2 are both primary products of propane oxidation.

While these data indicate that propane is oxidized in parallel to propylene and CO_x, they do not imply that CO_x cannot be produced also as a secondary product, i.e. by the sequential oxidation of propylene. Indeed, propylene should be significantly more reactive than propane, and deep oxidation to CO_x is expected. In order

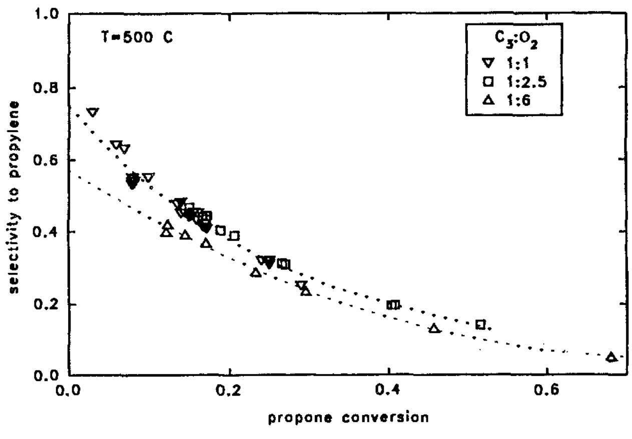

Fig. 1. Propylene selectivity profiles in propane oxidation over $Mg_4V_2Sb_2O_x$.

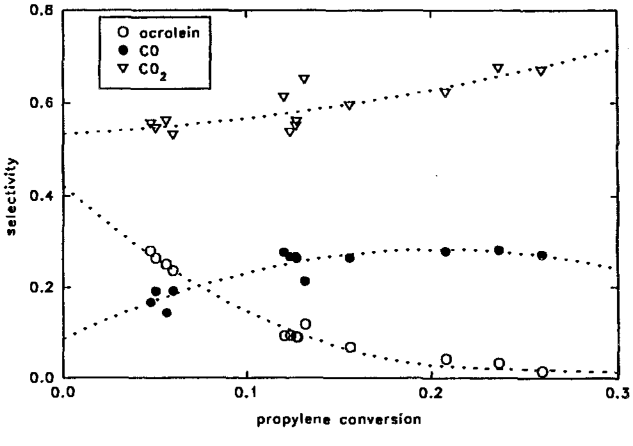

Fig. 3. Acrolein, CO, and CO_2 selectivity profiles in propylene oxidation over $Mg_4V_2Sb_2O_x$. $C_3^= : O_2 = 1 : 1$.

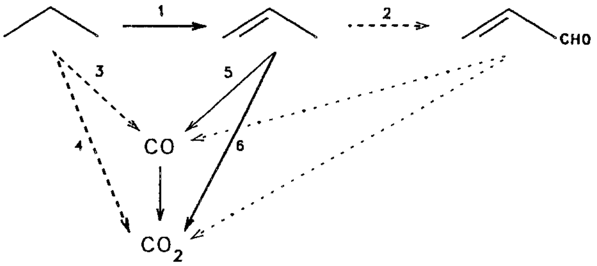

Fig. 4. Reaction network of propane oxidation over $Mg_2V_2Sb_2O_x$.

to clarify this part of the propane oxidation reaction network, the selectivity for propylene oxidation was measured over $Mg_4V_2Sb_2O_x$ at 460°C (fig. 3). CO_2 was found to be the major product formed, with smaller amounts of acrolein and CO detected as well. As shown in fig. 3, the selectivity to acrolein and CO_2 both extrapolate to non-zero values at zero propylene conversion. As in propane oxidation, extrapolation of the CO selectivity is not unambiguous. Here, the acrolein and CO_2 selectivities at zero conversion do not sum to 100%, indicating that the CO selectivity must also be non-zero at zero conversion. This conclusion is supported by additional measurements at still lower propane conversions [6].

The overall conclusion derived from the observed results is consistent with the reaction network shown in fig. 4, with the major reaction paths indicated by solid arrows. The primary reaction path is the oxidation of propane to propylene and subsequent oxidation of propylene to CO_x. Small amounts of acrolein are observed, as produced by the partial oxidation of propylene. An additional source of CO and CO_2 is the direct (non-sequential) deep oxidation of propane. And owing to the high reactivity of acrolein under the operating conditions used for propane oxidation, any acrolein, if produced at all, will be readily oxidized further to CO and CO_2. However, since acrolein was not detected directly as a product in propane oxidation, the expected reactions ensuing from this intermediate are shown only by dotted arrows in the reaction scheme (fig. 4).

The resulting conclusion, that two different sites might be responsible for waste formation, affords us the opportunity to further modify the $Mg_4V_2Sb_2O_x$ composition through substitution, electronic doping, adjustment of acid–base and redox properties, and by structural site isolation of the paraffin activating sites [4,6,7].

4. Conclusions

An analysis of the reaction network of propane oxidation over $Mg_4V_2Sb_2O_x$ indicates that propylene is the only primary produced useful product, and that CO_x is produced largely by the sequential oxidation of the in situ produced intermediate propylene, and to a lesser extent by a parallel route of direct deep oxidation of propane. The presence of two parallel pathways to CO_x is of some interest, as it suggests that partial and deep oxidation may occur at different surface sites or involve different forms of reactive oxygen. Therefore, the catalysts should be amenable to further electronic modification via substitution or doping, to attain higher yields of useful products, or by site isolation of the paraffin activating centers [4,6]. It is clear that further modification of this catalyst is required to reduce CO_x formation. Studies are underway to achieve this objective.

In a separate investigation, the reaction kinetics of propane oxidation over $Mg_4V_2Sb_2O_x$ are reported [6].

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