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Regeneration studies of redox catalysts

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ABSTRACT

Cited advantages of circulating fluidized bed reactors (CFB) include higher selectivity and conversion together with the ability to optimize the process conditions of each vessel independently—temperature, gas partial pressure and residence time. DuPont commercialized a CFB process to produce maleic anhydride in which a vanadium pyrophosphate (VPO) was cycled between a fast bed riser and an air fed regenerator. Together with VPO, we examined two other redox catalyst systems—MoVSb (acrylic acid from propane) and FeMoO (methanol to formaldehyde).

The lattice oxygen capacity of the FeMoO catalyst was about five times higher than either the VPO or MoVSb with little adsorbed carbon but a significant quantity of chemisorbed water. Above 350 °C, carbon deposition was detected and increased with increasing temperature. Carbon deposition decreased with increasing temperature for the MoVSb system and its lattice oxygen capacity was slightly higher than for VPO. The carbon deposition pattern for VPO was the opposite of the MoVSb and increased with temperature. Based on a hydrogen and carbon mass balance during the catalyst re-oxidation treatment, the molecular composition of the adsorbed species were C_4H_6 and C_3H_3—like for the VPO and MoVSb, respectively. Based on the high lattice oxygen capacity, the formaldehyde reaction appears to be ideally suited for development in a CFB. Whereas the lattice oxygen contribution of the MoVSb is equivalent to VPO, less oxygen is required to produce acrylic acid (compared to maleic anhydride) so the incentive of developing a CFB process should be greater than for butane oxidation to maleic anhydride.

1. Introduction

Circulating solids between two reaction zones is a key characteristic of several new processes that are at the development stages, including methane combustion by a metal oxide (chemical looping combustion), post combustion capture of CO_2 from flue gas, hot gas cleaning to scavenge sulphur, and the methanol-to-olefins process to combust carbon that builds up in the catalyst pores. The advantages of circulating catalyst are related to selectivity and conversion together with the possibility of optimizing the reduction and oxidation conditions (temperature, gas partial pressures and residence time) (Patience and Lorences, 2006). However, the disadvantages must be considered and include: additional vessels (investment), catalyst cost, and operational complexity. The successful commercialization of a redox process requires an efficient regeneration step—fast reaction kinetics and a high lattice oxygen capacity. Furthermore, carryover of carbon species should be minimized.

DuPont commercialized a circulating fluidized bed reactors (CFB) process to produce maleic anhydride from butane in which a vanadium pyrophosphate (VPO) was cycled between an air fed regenerator and a fast bed riser with a highly reducing atmosphere (Contractor, 1999). Two other catalytic reactions that have redox properties include propane to acrylic acid using a mixed metal oxide, MoVSb (Dubois et al., 2006) and methanol to formaldehyde with a FeMoO (Soares-Vieira et al., 2004). The objective of this work is to evaluate the redox properties of the three systems—VPO, MoVSb, FeMoO. By comparing the lattice oxygen contribution as well as carbon deposition of the MoVSb and FeMoO to VPO, we can assess their potential for success in a CFB process.

2. Experimental

2.1. Catalysts

We used three different mixed-oxide catalysts: VPO from DuPont that was produced at a commercial scale for their *n*-butane to maleic anhydride CFB process; a mixed metal oxide—MoVSb—prepared by Arkema for the propane to acrylic acid process; and, an iron molybdate doped catalyst—FeMoO—fabricated

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Table 1
Main characteristics of catalysts.

Abbreviation used	Main active phase	Density (kg/m^3)	Average particle size (μm)
VPO	$(VO)_2P_2O_7$	800	177
MoVSb	$Sb_2Mo_{10}O_{31}/Sb_4Mo_{10}O_{31}$	1472	67
FeMoO	$Fe_2(MoO_4)_3$	881	176

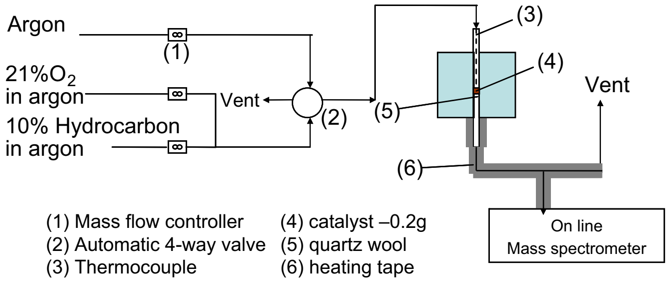

Fig. 1. Experimental set-up.

by Haldor Topsøe for the methanol to formaldehyde process. Each of these catalyst systems have redox characteristics in which lattice oxygen has been identified as a prime factor in achieving high conversion and selectivity. Their bulk characteristics are summarized in Table 1: the VPO and FeMoO have similar particle density and particle size while the MoVSb is much denser and the particle size is smaller.

X-ray diffraction analysis—Phillips X'Pert diffractometer equipped with a graphite monochromator, employing CuKα radiation $\lambda = 1.5418$ Å—was carried out to check the crystallinity, purity and active phase of each powder. For VPO, all the main peaks were indexed to the $(VO)_2P_2O_7$ structure, which considered to be the main active phase for VPO catalyst (Hutchings, 1991). Concerning the MoVSb, the predominant phase was M1 with a minor concentration of M2. The M1 phase is considered to be selective for acrylic acid (Millet et al., 2003). With the FeMoO, both $Fe_2(MoO_4)_3$ and MoO_3 phases were detected (Soares-Vieira et al., 2004).

2.2. Set-up

The experiments were carried out in a micro-fixed bed reactor coupled with an on-line Hiden quadropole mass spectrometer (MS). Both the exit and entrance configurations were modified in order to minimize gas diffusion in the feed lines and avoid condensation in the exit lines. Fig. 1 illustrates the feed manifold together with the reactor and MS. Argon was fed continually and either went to the vent or to the reactor. The procedure was as follows:

(1) Feed hydrocarbon during a sufficiently long period such that the hydrocarbon conversion reached a steady value.
(2) Purge the reactor with argon for 2 min and during this time, switch the feed from hydrocarbon to a mixture of oxygen/argon.
(3) Switch four way valve such that the oxygen/argon mixture goes to the reactor (and the argon goes to vent).
(4) After 4 min switch the four way valve again to purge the reactor with argon for 2 min.
(5) Switch the four way valve to send the oxygen/argon mixture to the reactor to evaluate the gas phase hydrodynamics.

All reactants and products were detected in real time with the MS at a frequency of 400 ms. Argon was used as the inert (instead of nitrogen) to minimize the overlap at 28 amu, which allows us to follow the evolution of CO with a greater precision. The contribution from the CO_2 cracking and reaction on the filament to the 28 amu was also taken into consideration as was all other secondary cracking patterns for the hydrocarbons. Their contributions were estimated by a series of calibration in which calibration gases were injected in the MS. We monitored Ar, H_2O, CO, CO_2, O_2, H_2, and hydrocarbon. Only for the case of the methanol to formaldehyde did we detect the presence of hydrogen during the reduction step.

All experiments were conducted at a volumetric flow rate of 25 ml/min (STP) and at characteristic temperatures for each process: 370, 400 and 425 °C for VPO; 320, 350, 375, 400, 425 °C for the MoVSb; and, 270, 300, 325, 350, 375, and 400 °C for the FeMoO. The temperature range for VPO was selected based on work by Hutchings (1991), Contractor (1999) and Lorences et al. (2004). Vitry et al. (2003), Védrine et al. (2003), and Dubois et al. (2008) recommend temperatures between 350 and 400 °C for MoVSb catalysts. FeMoO catalyst are most commonly used in fixed bed reactors in which hot spots of over 100 °C are possible (Patience and Cenni, 2007; Wachs and Briand, 2000) and the feed temperature might be as low as 270 °C (Bowker et al., 2008; Soares-Vieira et al., 2004; Jacques et al., 2006; House et al., 2007).

3. Results

The stoichiometry of the three reactions studied is as follows:

$$C_4H_{10} + 3.5O_2 \rightarrow C_4H_2O_3 + 4H_2O \quad \Delta H = -1240\ \text{kJ/mol}$$

$$C_3H_8 + 2O_2 \rightarrow C_3H_4O_2 + 2H_2O \quad \Delta H = -703\ \text{kJ/mol}$$

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow HCHO + H_2O \quad \Delta H = -156\ \text{kJ/mol}$$

Butane oxidation requires significantly more oxygen to make maleic than propane requires for acrylic acid or methanol needs for formaldehyde. The trend in heat of reaction is the same as for the oxygen demand and the cooling requirements for butane oxidation are an order of magnitude greater than for methanol oxidation on a molar basis. It is about twice as much on a mass basis (assuming 100% selectivity). Multi-tubular fixed bed reactors are the standard commercial technology for both propylene oxidation to acrolein and then to acrylic acid and for methanol to formaldehyde. Both multi-tubular fixed beds and turbulent fluidized beds are now practiced commercially to produce maleic anhydride.

3.1. VPO re-oxidation

The catalyst was initially reduced by a stream of 10% butane and 90% argon at 25 ml/min in the absence of molecular oxygen. The reduction/re-oxidation cycle is presented in Fig. 2. Butane conversion was high during the first several seconds and dropped off rapidly. We attribute the drop in conversion to the loss of labile lattice oxygen and due to the blocking/chemisorptions of hydrocarbon species to the active sites. The CO_2 and CO peaks rise very rapidly during the first couple seconds of reduction and reach a peak of nearly 3% and then drop to below 0.4% after a minute. Note that the level drops slowly thereafter, indicating that the catalyst is still active. The water trace follows the same trend as the carbon oxides. During the reduction, the CO/CO_2 ratio was close to 1 and it was about the same at each of the three temperatures tested.

The chemisorbed carbon (and hydrogen) from the reduction step remains on the catalyst during the 4 min argon purge. As soon as we switched the feed gas from argon to the oxygen/argon mixture, significant quantities of CO_2, CO and H_2O are detected. As shown in