Structural Characterization of Niobium Phosphate Catalysts used for the Oxidative Dehydrogenation of Ethane to Ethylene

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Vanadium phosphorus oxides (V-P-O) represent the most well studied heterogeneous complex oxide catalyst system. Thousands of articles have been published regarding their preparation routes, the nature of the active vanadium phosphate phase and their reaction mechanisms. A related group of compounds, niobium phosphates (Nb-P-O), are now also beginning to receive some attention from academic researchers.[1]

Ethylene (C_2H_4) is one of the most important building blocks in chemistry, and ranks as one of the highest volume organic chemicals produced in the world.[2] Its demand is commercially met through an energy-intensive process, namely the steam-cracking of hydrocarbons (mainly naphtha and ethane). The oxidative dehydrogenation (ODH) of ethane (C_2H_6) to ethylene (C_2H_4) is a reaction that offers both energy and cost saving advantages over traditional steam-cracking technologies. However, before this process can be considered as a viable alternative to the current industrial process, a catalyst producing a high ethylene yield needs to be developed. We have found that niobium phosphate materials show good activity and excellent selectivity for this reaction. The objective of this study is to systematically explore the catalytic performance, structure and active phases present in the Nb-P-O system during the ODH of ethane into ethylene in order to better understand the structure/activity relationships that exist in the Nb-P-O catalyst system.

Three different Nb-P-O catalysts, namely NbP-1, NbP-2 and NbP-3, prepared in this study are shown in Scheme 1. The catalytic activities of three materials were determined at atmospheric pressure at a reaction temperature of 500 ºC, using a fixed bed quartz tubular reactor, in which the feed consisted of a mixture of $C_2H_6/O_2/He$ with a molar ratio of 30/10/60. The materials after activation and catalytic testing are denoted as NbP-1E, NbP-2E and NbP-3E, respectively.

From X-ray diffraction analysis the NbP-1 sample consists of a cubic $Nb_2P_4O_{15}$ phase, whilst NbP-2 is comprised of tetragonal $NbOPO_4$. The sample NbP-3, which is prepared by reducing NbP-2 in hydrogen, matches best to an orthorhombic $Nb_{1.91}P_{2.82}O_{12}$ phase. Catalytic testing shows that the order of selectivity to ethylene at 5% ethane conversion is NbP-3E (95%) > NbP-2E (85%) > NbP-1E (78%). NbP-3E also shows the highest activity, followed by NbP-2E and then NbP-1E.

SEM and TEM studies show that after catalytic testing both NbP-1E and NbP-2E catalysts largely retain the morphologies exhibited by their precursor materials. Catalyst NbP-1E shows a major morphology having a porous structure (Fig. 1(a)) and a minor morphology exhibiting characteristic sintered pores (Fig. 1(b)). Catalyst NbP-2E shows layer-type platelets (Fig. 1(c)) composed of small primary particles (Fig. 1(d)). On the other hand, sample NbP-3 exhibits a dramatic morphological change after catalytic testing. In the fresh catalyst, highly angular $Nb_{1.91}P_{2.82}O_{12}$ platelets (Figs. 2(a),

(b)) and more irregularly shaped platelets (Figs. 2(c), (d)) are found. The angular platelets retain their morphology and crystalline structure in the used sample (Fig. 2(e)) whereas the irregular platelets, which are believed to be the partially transformed $NbOPO_4$ (Fig. 2(d)) transform into smaller $Nb_{1.91}P_{2.82}O_{12}$ particles (as arrowed in Fig. 2(e) and shown at atomic resolution in Fig. 2(f)). From the above studies, it is shown that the $Nb_2P_4O_{15}$, $NbOPO_4$ and $Nb_{1.91}P_{2.82}O_{12}$ phases are all somewhat active for catalyzing the oxidative dehydrogenation of ethane to ethylene, with the $Nb_{1.91}P_{2.82}O_{12}$ phase being the most active and selective to ethylene formation.

References

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[2] A.M. Thayer, *Chemical & Engineering News* **74** (1996) 15.
[3] The authors gratefully acknowledge financial support from the NSF - Materials World Network Program (Grant # DMR-0709887).
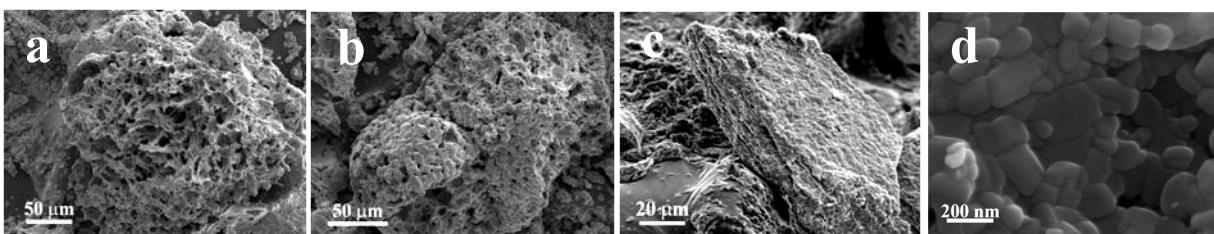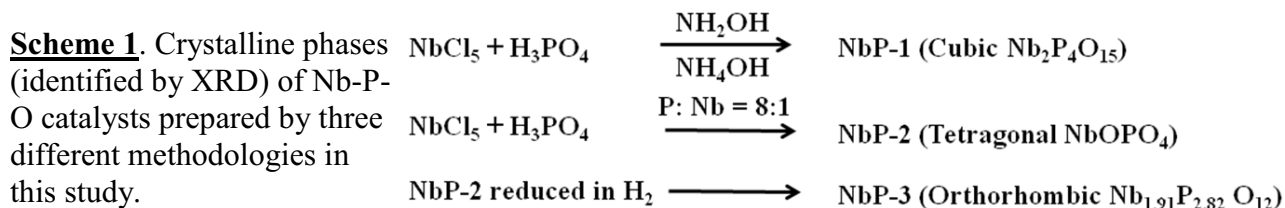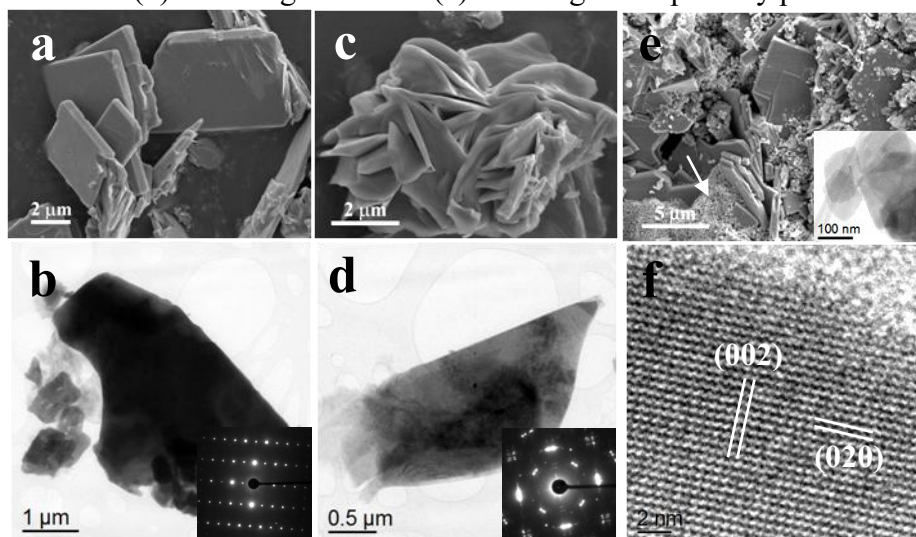
Scheme 1. Crystalline phases (identified by XRD) of Nb-P-O catalysts prepared by three different methodologies in this study.

$$NbCl_5 + H_3PO_4 \xrightarrow[\text{NH}_4\text{OH}]{\text{NH}_2\text{OH}} \text{NbP-1 (Cubic } Nb_2P_4O_{15})$$

$$NbCl_5 + H_3PO_4 \xrightarrow{\text{P: Nb = 8:1}} \text{NbP-2 (Tetragonal } NbOPO_4)$$

$$\text{NbP-2 reduced in } H_2 \longrightarrow \text{NbP-3 (Orthorhombic } Nb_{1.91}P_{2.82}O_{12})$$

Figure 1. (a, b) SEM micrographs of sample NbP-1E showing (a) an agglomerate of a porous structure and (b) a minor amount of a sintered structure; (c, d) SEM micrographs of sample NbP-2 showing (c) a layer-type structure and (d) an enlargement of 1(c) showing small primary particles.

Figure 2. (a, b, c, d) SEM (*column 1*) and BF TEM (*column 2*) micrographs of sample NbP-3 showing (a, b) clusters of angular $Nb_{1.91}P_{2.82}O_{12}$ platelets (inset; SADP in 2b corresponds to [100] $Nb_{1.91}P_{2.82}O_{12}$); (c, d) irregularly shaped platelets (inset; complex overlapping SADP's in 2(d) correspond to partially transformed tetragonal $NbOPO_4$ crystals); (e) an SEM micrograph of NbP-3E showing both angular platelets and smaller particles (as arrowed and as shown in the inset BF TEM micrograph); and (f) an HRTEM micrograph of a smaller particle in 2(e) showing the (002) and (020) planes in the [100] projection of $Nb_{1.91}P_{2.82}O_{12}$.