Harold and Samuel first described the selective oxidation of isobutane with heteropoly catalysts in 1979 [1]. Later, several research groups carried out the oxidation of isobutane catalyzed by heteropoly compounds [2–11]. Many investigations have been done on the modification of molybdophosphoric salts with the Keggin structure. The salts can be modified by substituting protons with potassium or cesium, substituting transition metal ions such as \( \text{Cu}^{2+} \), \( \text{Fe}^{3+} \), \( \text{Ni}^{2+} \) for counter-cations, or by altervalent replacement (typically V-substitution for Mo). Improvement of catalytic behavior can be observed due to an effective modification process. In addition, other catalytic systems, such as \( \text{V} / \text{MCM-41} \) and Te—Mo-based mixed oxides have also been used as catalysts for this reaction [12–20]. It has been found that high selectivity to methacrolein (MAL) can be achieved over Te—Mo-based mixed oxide catalysts, while high selectivity to methacrylic acid (MAA) was observed with heteropoly compounds.

Earlier we were able to show that tellurium is a very important element that serves to achieve high selectivity to MAL, whereas a phase containing V–Te\(^{4+}\) is active and selective component in the Mo—V—Te-based oxide catalysts for selective oxidation of isobutane to MAA [12–15]. The mixed oxide catalysts appear to have a multifunctional surface structure; Mo\(^{6+}\) or V\(^{5+}\) ions are responsible for the activation of isobutane and abstraction of methylene hydrogen, while the abstraction of the methyl hydrogen and \( \alpha \)-hydrogen (from isobutene) is associated with Te\(^{4+}\) cation and the chemisorption of olefin and insertion of oxygen occur on Mo\(^{6+}\) ion [12, 21, 22]. However, available information is not sufficient to understand the effect of Te in the heteropoly compounds on the activity and selectivity of catalysts in the partial oxidation of isobutane. Especially the role of Te in V-substituted heteropoly compound system is far from being understood.

The aim of the work reported here was to explore the ways leading to improvement of selectivity to a desired product in the oxidation of isobutane over heteropolyacid catalysts.

**EXPERIMENTAL**

**Catalyst Preparation**

A series of \( \text{H}_3^{+}\text{PMo}_{12−x}\text{V}_x\text{O}_{40} \) \((x = 0–3)\) heteropoly compound catalysts was prepared using already described methods [23]. In a typical synthesis, 7.1 g of \( \text{Na}_2\text{HPO}_4 \) was dissolved in 100 mL water and mixed with \( \text{NaVO}_3 \) that had been dissolved in 100 mL of hot water. The mixture was cooled and acidified to a red color with 5 mL of concentrated sulfuric acid. To this mixture a solution of \( \text{TeO}_2 \) was added dropwise, followed by the addition of aqueous solution of cesium carbonate at \( 80^\circ\text{C} \). The resulting suspension or solution was evapo-
rated to dryness at 80°C. The powder samples were collected, dried at 110°C for 12 h, and then calcined at 320°C for 2 h. The actual composition of the samples may be $\text{Cs}_2\text{Te}_{0.2}\text{H}_{x}\text{PMo}_{12-x}\text{V}_x\text{O}_n$, but in this paper the catalysts are designated as $\text{Cs}_2\text{Te}_{0.2}\text{H}_{y}\text{PMo}_{11}\text{VO}_n$.

**Catalyst Characterization**

Powder X-ray diffraction patterns (XRD) were collected using a Shimadzu XRD-6000 scanning (4°/min) with Cu$K_\alpha$ radiation (40 kV, 30 mA). The Fourier transform infrared spectra (FT-IR) were recorded at room temperature using a NICOLET Impact 410 spectrometer. Specific surface areas of the catalysts were computed using the BET adsorption isotherms of $N_2$ measured at $-196°C$ (Microneritics ASAP2010). Scanning electron micrographs (SEM) were taken through a FESEM XL-30 field emission scanning electron microscope. X-ray, photoelectron spectra (XPS) were recorded on a VG ESCA LAB MK-II. X-ray electron spectrometer using AlK$_\alpha$ radiation (1486.6 eV, 10.1 kV). The binding energies for the samples in spectra were referenced to the $\text{Al}_2\text{O}_3$ line at 284.7 eV. The measurement error of the spectra was ±0.2 eV.

**Catalytic Tests**

The reaction was performed in a stainless steel tubular fixed bed reactor (16 mm i.d., 400 mm long) at atmospheric pressure. A mass flow controller regulated reaction feed, and a mini—pump fed water. The catalytic reaction conditions was as follows: molar ratio of the feed gas $i$-$\text{C}_4\text{H}_{10}$ : $\text{O}_2$ : $\text{N}_2$ : $\text{H}_2\text{O} : 1$ : $1$ : $2$ : $1$, gas hourly space velocity 1000 mL h$^{-1}\text{g}^{-1}\text{cat}$. The experiments were carried out at 350°C. The products were then fed via heated lines to an on-line gas chromatography for analysis. Methacrolein, methacrylic acid, CO$_3$ (CO, CO$_2$), and acetic acid (HAC) were the main products. Mass balance of carbon ≥97% was typically observed.

**RESULTS AND DISCUSSION**

**XRD and FT-IR Studies**

The X-ray diffraction patterns of the $\text{Cs}_2\text{Te}_{0.2}\text{H}_{0.6+x}\text{PMo}_{12-x}\text{V}_x\text{O}_n$ heteropoly compounds are shown in Fig. 1. Only the diffraction lines typical to molybdophosphoric salts with, a cubic structure [2–6] were present on. The diffractograms. No peaks due to MoO$_3$ were observed on the XRD patterns.

The FT-IR spectra of catalysts are compared in Fig. 2. The bands at 2847, 1466 and 797 cm$^{-1}$ can be readily seen which, are characteristic of a Keggin structure [2—6].

The SEM images of $\text{Cs}_2\text{Te}_{0.2}\text{H}_{0.6+x}\text{PMo}_{12-x}\text{V}_x\text{O}_n$ and $\text{Cs}_2\text{Te}_{0.2}\text{H}_{3.6}\text{PMo}_9\text{V}_3\text{O}_n$ are shown in Fig. 3. Sphere morphology of the samples can be easily recognized. The average particle size of the $\text{Cs}_2\text{Te}_{0.2}\text{H}_{0.6}\text{PMo}_{12}\text{V}_x\text{O}_n$ spheres near to 1.1 μm can be estimated, while the average particle size of the $\text{Cs}_2\text{Te}_{0.2}\text{H}_{3.6}\text{PMo}_9\text{V}_3\text{O}_n$ spheres appears to be about 2.6 μm.

Table 1 shows the specific surface area ($S_{\text{BET}}$) of the catalysts. It can be seen that for all samples the surface area of the $\text{Cs}_2\text{Te}_{0.2}\text{H}_{0.6+x}\text{PMo}_{12-x}\text{V}_x\text{O}_n$ catalysts gradually decreases with increasing level of substitution of Mo by V. Moreover, the $S_{\text{BET}}$ values slightly decrease as the content of Cs in the $\text{Cs}_2\text{Te}_{0.2}\text{H}_{0.6}\text{PMo}_{12}\text{V}_x\text{O}_n$ catalyst increases.

To gain further insight into the surface structure and properties of these heteropoly compounds. XPS spectra of Cs 3d$5/2$, Mo 3d$5/2$, V 2p$3/2$, Te 3d$5/2$ and P 2p