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Review

Kinetics and mechanism of gas phase MTBE and ETBE formation on Keggin and Wells–Dawson heteropolyacids as catalysts

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ABSTRACT

The paper reviews the work of the authors concerning the mechanism and kinetics of catalytic gas phase formation of tertiary ethers: methyl-*tert*-butyl ether (MTBE) and ethyl-*tert*-butyl ether (ETBE). The mechanism of tertiary ethers synthesis from alcohol and isobutene was proposed. Basing on the sorption of reagents and IR investigations the elementary steps of reactions were proposed. As the rate determining step two possible reactions: formation of carbocation and formation of ether from alcohol supplied from the bulk and protonated isobutene were discussed. The general rate equation was formulated.

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Contents

1. Introduction

Heteropolyacids (HPA) of Keggin type such as $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ belong to the oxometallates which have found industrial applications as both acid–base and redox catalysts. In last decades they have been used in the industrial hydration of propene, *n*-butene, isobutene [1,2], polymerization of tetrahydrofurane [3] as well as the oxidation of methacrolein to methacrylic acid [4]. This is due to their specific physicochemical properties. In the solid state and in solution they exhibit very high acidity and in fact they belong to the strongest mineral acids comparable to that of $HClO_4$, CF_3COOH and so called superacids. Some of them are also relatively strong oxidation agents. Another important property of solid HPAs is their high sorption capacity comprising not only chemisorption on the external surface of crystallites but also absorption in their bulk. The latter property is limited to the polar molecules such as water, ammonia, alcohols, and aldehydes. The non-polar molecules may be adsorbed only on the external HPA crystallites surface. The penetration of the bulk of crystallites by polar molecules is generally fast and frequently accompanied by the protonation with the protons loosely bonded in hydrogen bonds between HPA anions. The absorbed molecules are mobile in the crystal lattice similarly as the molecules in the liquid and hence the crystal with absorbed molecules is frequently described as "pseudoliquid state".

Besides dodeca-heteropolyacids of Keggin structure, similar (Fig. 1a) catalytic properties exhibit also octadeca-heteropolyacids of Wells–Dawson structure mainly, $H_6P_2W_{18}O_{62}$ (Fig. 1b). $H_6P_2W_{18}O_{62}$ shows somewhat higher catalytic activity than the strongest and highly active Keggin type $H_3PW_{12}O_{40}$ and this is why it is now investigated in many laboratories [5].

HPA anions are forming the so called primary structure of crystalline HPA. The anions, the counter cations (metal atoms or protons) as well as the absorbed molecules are forming the secondary structure. In the free solid heteropolyacid protons are forming hydrogen bonds between anions. They are relatively weakly bonded and can be easily used for the protonation of absorbed polar molecules or their clusters. Tertiary structure is the structure of solid heteropoly compound as assembled: the size of the primary and secondary particles, pore structure, distribution of protons and cations, etc. [6].

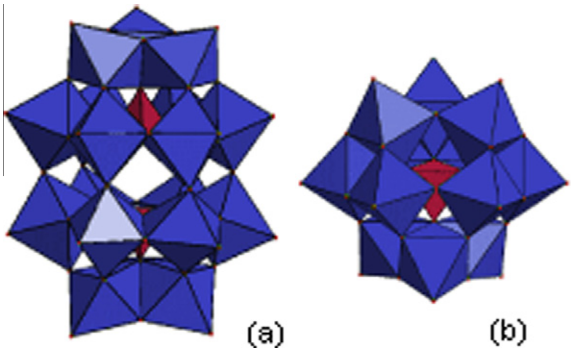

Fig. 1. Anions of (a) Keggin type structure. (b) Wells-Dawson type structure.

The importance of the pseudoliquid phase in HPAs for the catalysis has been stressed by Misono in his numerous papers [7,8]. According to him catalytic reactions occurring on heteropolyacids can be classified as:

1. Surface reactions in which no penetration of reagents into the bulk of HPA crystallites occurs. The chemisorbed molecules are interacting only with the surface atoms of the crystallites and those of the bulk are not involved into the catalytic process. Cracking of the non-polar cumene can be cited as an example of such kind reaction [9].
2. Bulk type I reaction, in which the polar molecules of the substrate penetrate the bulk of HPA crystallites where their transformation occurs and the products are given off to the external gas or liquid phase. In this case diffusion and reaction in the bulk are faster than the reaction on the external surface. A typical example of such reaction taking part in the pseudoliquid phase is the dehydration of ethanol [10].
3. Bulk type II reaction, in which the non-polar reagent remaining at the surface reacts with some species, e.g. electrons or protons, supplied from the bulk. This may be acid–base or redox type catalytic reaction.

It should be observed that Misono's classification does not comprise the case when there are two substrates of catalytic reaction one of them being polar and penetrates the bulk of the crystal lattice while the other one non-polar substance remains adsorbed at the surface. The study of such reaction has been undertaken by the present authors and the main results are reviewed in the present paper. In particular it concerns the catalytic formation of tertiary ethers in gas phase by the addition of polar alcohols, methanol or ethanol, to non-polar isobutene. Reaction of the formation of methyl-*tert*-butyl ether (MTBE) [11] was studied using solid silicododecatungstic acid, $H_4SiW_{12}O_{40}$, and formation of ethyl-*tert*-butyl-ether (ETBE) [12] using solid diphosphooctadecatungstic acid, $H_6P_2W_{18}O_{62}$. Both ethers have found practical application as the antiknocking components in lead free automotive fuels. Due to some reservations from the environmental reasons, MTBE is no more largely used and is mostly substituted by ETBE.

$H_4SiW_{12}O_{40}$ belongs to the strongest acids in Keggin type series and deserves attention due to its relatively high thermal decomposition temperature. In more recent time $H_6P_2W_{18}O_{62}$ became the object of increased interest in the literature as it appeared to be more active catalyst than $H_3PW_{12}O_{40}$ the strongest Keggin type acid.

Due to the fact that kinetics of catalytic reactions on solid heteropolyacids has been only rarely studied in details we decided to concentrate our research in the study of mechanism and kinetics of both catalytic reactions. Our work comprised three stages. The first of them comprised such physicochemical properties as sorption capacity of the catalysts, their thermal stability, IR spectra of adsorbed or absorbed molecules, etc. In the second stage reaction