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Mendeleev Commun., 2021, **31**, 712–714

Mendeleev Communications

Gas-phase oxidative carbonylation of methane to acetic acid over zeolites

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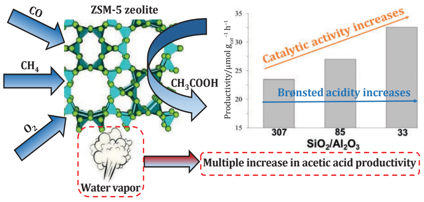
DOI: 10.1016/j.mencom.2021.09.040

Gas-phase oxidative carbonylation of methane was first performed on ZSM-5 zeolites. The addition of water vapor to a mixture of carbonylation gases leads to a multiple (by two orders of magnitude) increase in acetic acid yield. Zeolites with high acidity, primarily Brønsted acidity, favor the target product formation.



Keywords: acetic acid, ZSM-5 zeolites, oxidative carbonylation of methane, acidity, water vapor.

Acetic acid (AA) is one of the most important intermediate petrochemicals used in the production of vinyl acetate, cellulose acetate, acetic anhydride, acetyl chloride, terephthalic acid, chloroacetic acid and other chemicals necessary for the manufacturing of final products applied as plasticizers, stabilizers, fibers, films, adhesives, dyes, solvents, detergents and so on. The global production of AA in 2020 amounted to almost 19 million tons, and by 2023, according to experts, it will grow to 21.7 million tons.[1,2] Approximately 80% of AA production capacity is based on gas feedstock and uses a multistage scheme for converting natural gas to AA, applying the Monsanto^{TM}, Celanese^{TM}, Acetica^{TM} and Cativa^{TM} processes.[3–7] These include steam reforming of methane to produce syngas (a mixture of CO and H_2) and then methanol with its subsequent carbonylation on homogeneous rhodium or iridium catalysts, promoted with iodine-containing compounds.

The main disadvantage of the currently existing industrial processes for producing AA by carbonylation of methanol is their multistage nature. Over the past decades, the scientific community has sought to simplify this complex transformation scheme by developing various methods for the direct oxidative conversion of methane to this valuable product applying diverse oxidizing agents such as sulfuric acid,[8] potassium peroxodisulfate solution in trifluoroacetic acid,[9] nitrous oxide,[10] carbon dioxide[11–13] and carbon monoxide + oxygen.[14,15] The first three of these methods[8–10] involve the use of expensive and toxic reagents in combination with aggressive reaction media, while the direct conversion of methane and carbon dioxide to AA, in turn, is challenging due to their high activation energies. In this regard, the oxidative carbonylation of methane with more active carbon monoxide and oxygen is of great interest:

$$CH_4 + CO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH,\ \Delta G^0_{298\,K} = -212.2\ \text{kJ mol}^{-1}. \quad (1)$$

However, in the absence of oxygen, AA was found among the products of methane and carbon monoxide conversion over Zn/ZSM-5 at 500 °C only as an adsorbed intermediate.[16] Until recently, the oxidative carbonylation of methane (equation 1) was carried out under homogeneous conditions at low temperatures (80–95 °C) in the presence of complexes of noble metals (Rh, Pt, Pd and Au).[17–19] Still, the metal complexes exhibited noticeable activity either in an acidic medium such as trifluoroacetic and perfluorobutyric acids or in the presence of hydrohalic acids such as HI and HCl, which did not make these conditions production-oriented.

In the last few years, there have been reports on the synthesis of AA from CH_4, CO and O_2 under liquid-phase conditions on zeolites dispersed in water and modified with various metals (copper, Group VIII metals).[14,15,20,21] In contrast to metal complexes, such systems are free of acid promotion and are easily separated from the reaction products. The reaction is carried out at 150–200 °C and a pressure of 7 MPa in a batch-type autoclave reactor. However, the batch running is associated with a poor space–time yield of the target product. A method for producing AA by oxidative carbonylation of methane in a continuous mode, when all reactants are in the gas phase, appears very promising. According to the published data,[22] carbonylation occurs mainly on the Brønsted acid sites (BAS). For the oxidative carbonylation of methane, it was shown that the carbonylation activity increases in the presence of BAS traces.[21]

In this communication, we present the results of gas-phase oxidative carbonylation of methane for the production of AA in a flow reactor using ZSM-5 zeolites with different SiO_2/Al_2O_3 molar ratios (HCBV-30, HCBV-80 and HCBV-300, where the number means SiO_2/Al_2O_3) and, accordingly, different densities of acid sites. The reaction was investigated at temperatures of 250–450 °C and a pressure of 6.5 MPa in the GHSV range of 1250–40000 h^{-1}.

To exclude the potential contribution of metal components present in the zeolite structure, the elemental composition of the catalysts used was analyzed. According to the results (Table S1, see Online Supplementary Materials), it can be argued that the zeolite samples used are pure materials, and the trace metal impurities therein cannot significantly affect the catalysis. The description of the catalytic experiments, the initial mixture composition and the nitrogen adsorption data (Table S2) for the catalysts used are given in Online Supplementary Materials.

The densities of total acidity sites, BAS and Lewis acid sites (LAS) in zeolite catalysts were determined using temperature-programmed desorption of ammonia (NH_3-TPD) and Fourier-transform infrared spectroscopy of adsorbed pyridine (Py-FTIR).

Table 1 The acidic properties of the used ZSM-5 zeolite catalysts containing medium (I) and strong (II) acid sites.

Catalyst	SiO_2/Al_2O_3	Amount of NH_3 desorbed/μmol g^{-1}			I/II	Density/μmol g^{-1}		BAS/LAS
		I	II	Total		BAS	LAS	
HCBV-30	33	593	500	1093	1.19	180	48	3.7
HCBV-80	85	270	297	567	0.91	142	14	10.1
HCBV-300	307	97	146	243	0.66	80	5	16.0

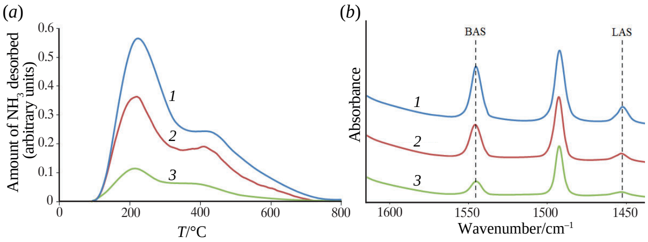


Figure 1 (*a*) NH_3-TPD and (*b*) Py-FTIR profiles of (*1*) HCBV-30, (*2*) HCBV-80 and (*3*) HCBV-300 zeolites with different SiO_2/Al_2O_3 molar ratios.

The NH_3-TPD and Py-FTIR spectra for all HCBV samples with different SiO_2/Al_2O_3 are shown in Figure 1. The data obtained from the spectra are summarized in Table 1.

As can be seen from Figure 1, in the NH_3-TPD spectra of HCBV samples in the range of 210–220 and 410–420 °C, two characteristic peaks of desorbed ammonia are observed, which are responsible for medium (I) and strong (II) acid sites, respectively, which together determine the total acidity of the zeolite. As follows from Table 1, with decreasing SiO_2/Al_2O_3 from 307 to 33, the density of acid sites I and II increases, which leads to an increase in the total acidity. At the same time, the I/II ratio also rises from 0.66 to 1.19. It should be noted that, according to Py-FTIR data, the catalysts used are characterized by different distributions of BAS and LAS, and the proportion of BAS is much higher than that of LAS, which, in turn, grows with an increase in the SiO_2/Al_2O_3. Thus, its increase from 33 to 307 is accompanied by an increase in the BAS/LAS ratio from 3.7 to 16.0.

The catalyst performance in the oxidative carbonylation of methane was investigated over a wide temperature range using the initial mixture without (dry mixture) and with the water addition (wet mixture). As illustrated in Figure 2, raising the temperature to 350 °C gradually increases the specific productivity for AA to 0.18 μmol g_{cat}^{-1} h^{-1}. The subsequent increase in temperature to 450 °C reduces the yield of the target product to 0.03 μmol g_{cat}^{-1} h^{-1} due to the acceleration of secondary transformations of AA, leading to polycyclic aromatic compounds, which are coke precursors.[16] On the contrary, when water is added to the initial mixture, the AA yield increases significantly. In the range of 250–450 °C, the specific productivity increases from 0.3 to 32.6 μmol g_{cat}^{-1} h^{-1}. Water conversion is in the range of 5–10%. Such an increase in the specific productivity for AA (by two orders of magnitude) when feeding a wet mixture is explained by the fact that water vapor accelerates the chemical desorption of AA due to the hydrolysis of the acyl intermediate. This explanation is consistent with experimental[14,23] and calculated[24] data.

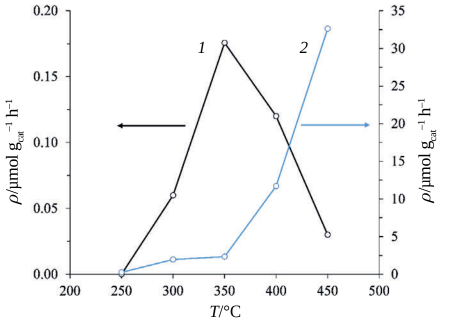


Figure 2 The specific productivity (*ρ*) for AA as a function of temperature in the conversion of (*1*) dry mixture CH_4–O_2–CO–N_2 (57 : 3 : 10 : 30, v/v) and (*2*) wet mixture CH_4–O_2–CO–H_2O (57 : 3 : 10 : 30, v/v) on the HCBV-30 catalyst at *P* = 6.5 MPa and GHSV = 1250 h^{-1}.

Since methane is in a large excess compared to other reaction mixture components, its conversion is slight and does not exceed 3%. The temperature dependence of the conversion of oxygen and carbon monoxide is shown in Figure S1 (see Online Supplementary Materials).

It should be noted that the major liquid products of the oxidative carbonylation of methane, in addition to AA, are methanol and acetone. Table S4 shows the specific productivity for oxygenates at various temperatures in the presence of HCBV-30 and the absence of a catalyst. As indicated in Table S4, the reaction on HCBV-30 proceeds to form methanol in high yield through the partial oxidation of methane. The total amount of methanol increases in the temperature range of 250–400 °C from 7.3 to 273.2 μmol g_{cat}^{-1} h^{-1}. At 450 °C, the yield of methanol drops to 138.4 μmol g_{cat}^{-1} h^{-1}, which is most likely caused by its decomposition followed by steam reforming to CO_2 and H_2. The specific productivity for acetone is negligible and is no more than 0.4 μmol g_{cat}^{-1} h^{-1}, and acetone begins to release only at 400 °C. Since the increase in temperature and the presence of water promote the primary reaction, all subsequent experiments were carried out at 450 °C under the conditions of feeding the wet mixture. To determine the effect of the acidity of the zeolite surface on the catalytic activity, we examined the HCBV-30, HCBV-80 and HCBV-300 samples, which have different SiO_2/Al_2O_3 and, thus, differ in the distribution and density of acid sites. The performance of catalysts for oxidation products is shown in Figure 3.

As presented in Figure 3, on decreasing the SiO_2/Al_2O_3 in zeolite from 307 to 33, the rate of target product formation increases. HCBV-30 exhibits the highest specific productivity for AA (32.6 μmol g_{cat}^{-1} h^{-1}) compared to HCBV-80 (27.0 μmol g_{cat}^{-1} h^{-1}) and HCBV-300 (23.5 μmol g_{cat}^{-1} h^{-1}). The enhanced activity of HCBV-30 correlates with its high acidity and mainly BAS density, consistent with the statement[21] that the Brønsted acidity of mordenite is directly related to the synthesis of AA from CH_4, CO and O_2.

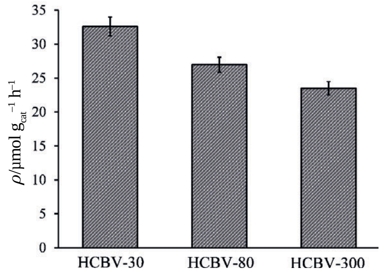


Figure 3 The specific productivity (*ρ*) for AA in the conversion of wet mixture CH_4–O_2–CO–H_2O (57 : 3 : 10 : 30, v/v) on zeolites with different SiO_2/Al_2O_3 molar ratios at *T* = 450 °C, *P* = 6.5 MPa and GHSV = 1250 h^{-1}.

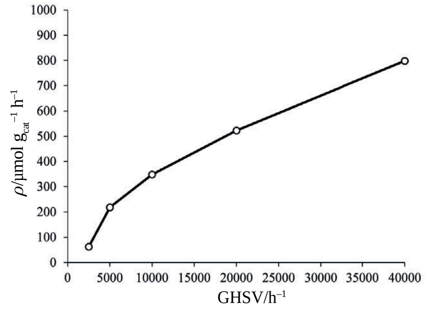


Figure 4 The specific productivity (ρ) for AA as a function of GHSV in the conversion of wet mixture CH_4–O_2–CO–H_2O (57 : 3 : 10 : 30, v/v) on the HCBV-30 catalyst at T = 450 °C and P = 6.5 MPa.

The influence of GHSV on the specific productivity for AA was investigated. An increase in GHSV in the range up to 40000 h^{-1} (Figure 4) is accompanied by a considerable increase in the specific productivity of the catalyst for AA to 798.5 μmol g_{cat}^{-1} h^{-1}, which is significantly higher than such values in several other studies.[15,24,25]

In summary, it was demonstrated for the first time that it is possible to obtain AA, whose specific productivity at GHSV of 40000 h^{-1} reaches 798.5 μmol g_{cat}^{-1} h^{-1}, by oxidative carbonylation of methane under gas-phase catalysis over zeolites. It was shown that the addition of water vapor contributes to a sharp (by two orders of magnitude) increase in the yield of the target product. A direct correlation was established between the degree of zeolite acidity, primarily the BAS density, and the AA formation.

This work was supported by the Russian Science Foundation (project no. 19-73-00254).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.040.

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Received: 23rd March 2021; Com. 21/6503