Aromatization of methanol and methylization of benzene over Mo₂C/ZSM-5 catalysts

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Introduction

The adsorption and reaction pathways of methanol have been investigated on various Mo_2C-containing catalysts, which have been characterized by XPS and surface acidity measurements. Previous studies demonstrated that depending on the reaction conditions and on the catalyst systems methanol can be transferred into olefins and aromatics on ZSM-5 zeolites [1, 2]. The latter process is promoted by Ga, and more particularly by Zn additive [1-3]. Recently it has been found that Mo_2C is an effective promotor in the aromatization of several hydrocarbons and ethanol occurring on ZSM-5 [4-5]. Moreover, this catalyst exhibited a unique behavior, as it can convert methane into benzene with 80% selectivity at 10-15% conversion, which ZSM-5 alone or promoted with Zn and Ga cannot do it [6-8]. Data obtained in the present work show that deposition of Mo_2C on ZSM-5 markedly enhances the formation of aromatics (benzene, toluene, xylene and C_9^+) from methanol.

Experimental

Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube (8 mm id) connected to a capillary tube [4]. The flow rate was in general 40 ml/min, but the reaction was also studied at different space velocities. The carrier gas was Ar, which was bubbled through the methanol at room temperature: its content was ~9.0%. Generally 0.3 g of loosely compressed catalyst sample was used. Reaction products were analysed by a gas chromatograph (HP 5890) equipped with PORAPAQ Q+S packed column by C_2H_6/H_2. All the catalyst samples have been characterized before by XPS. The binding energy for $Mo(3d_{5/2})$ fell in the range 227.7-228.2 eV, and for $C(1s)$ 283.8 eV. These values are consistent with those attributed to Mo_2C.

Results and Discussion

By means of FTIR spectroscopy we found that methanol interacted strongly with the highly dispersed Mo_2C on ZSM-5 at 300 K and gave rise to the production of methoxy species. At higher temperature the characteristic vibrations of dimethyl ether (band 2971 cm⁻¹) and di-σ-bonded ethylene (band at 2925 cm⁻¹) were also identified.

Mo_2C alone can not convert methanol into aromatics. It catalyzes only its decomposition to CO, H_2 and CH_4. The situation remained the same when Mo_2C was deposited on SiO_2 of high surface area. A completely different picture was found, however, on ZSM-5-based catalysts. ZSM-5 alone catalyzes the conversion of methanol to olefins, and to less extent to aromatics [1-3]. Its catalytic performance depends on the Si/Al ratio, or in other words on the number of Brönsted sites, which decreases with the increase of silica content. This is reflected in the production of aromatics: highest value was measured on ZSM-5(30) and the lowest one on ZSM-5(280). Adding Mo_2C to ZSM-5 samples significantly enhanced the formation of aromatics, particularly that of xylenes and C_9^+ on all zeolite samples. The best results were obtained at 5% Mo_2C content. The yield of total aromatics reached the value of 62% at 773 K. Further increase in the Mo_2C loading led to a decline of total selectivity of aromatics due to the marked decrease of Brönsted sites.

In the explanation of the promoting effect of Mo_2C we assume that Mo_2C opens a new route for the activation of methanol. In addition to O-H bond scission proceeding on ZSM-5, the cleavage of C-O bond of adsorbed CH_3OH on Mo_2C may also occur to yield CH_3 radical. The occurrence of this step in the dissociation of methanol has been recently confirmed by several spectroscopic tools on Pd(111) surface [9]. In subsequent reaction CH_3 species decomposes to CH_2, the recombination of which leads to the formation of ethylene. Another fraction of CH_3 species is hydrogenated into methane. The active sites for this step could be the carbon deficient site on the Mo_2C surface, which may have a high affinity towards oxygen. The reactivity of this site has been exhibited in the promotion of CO dissociation at 300 K and also in the scission of C-I bond in the adsorbed alkyl iodides. The role of the Mo_2C, however, is not accomplished by opening a new route for the activation of methanol to ethylene, as it also catalyzes its aromatization. It is very likely that Mo_2C provides dehydrogenation centres for adsorbed ethylene resulting in different products, which are converted on the acidic sites of ZSM-5 into aromatics.

In order to refine the picture further we compared the rate of formation of aromatics from methanol and ethylene on Mo_2C/ZSM-5(80) under exactly the same experimental conditions. We obtained that the aromatization process begins at lower temperatures and occurs much more rapidly from methanol than from ethylene. This suggests that the allylic and other C_xH_y species generated in the activation of methanol have a higher tendency and reactivity to be transformed into aromatics as compared to the "stable" ethylene molecule. Another important feature is that a larger amount of C_8-C_9^+ aromatics is formed in the reaction of methanol as compared to the reaction of ethylene. In the latter case C_9^+ aromatics was produced only in traces. The possible reason of the different product distribution is that the using methanol as starting reagent the methylization of benzene formed also proceeds. This assumption has been proved by the study of the methylization of benzene with methanol. While this process proceeds slowly on pure ZSM-5, it is greatly promoted by Mo_2C indicating the high reactivity of hydrocarbon fragments formed in the activation of methanol.

References

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