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PARTIAL OXIDATION OF ETHANE OVER K_2MoO_4/SiO_2 AND POTASSIUM PROMOTED MoO_3/SiO_2 CATALYST

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Silica supported K_2MoO_4 and potassium-promoted MoO_3 were used as catalysts for the partial oxidation of ethane in fix-bed continuous-flow reactor at 770–823 K using N_2O as oxidant. The main products of the oxidation reaction were ethylene, acetaldehyde, CO and CO_2. Addition of various compounds of potassium to the MoO_3/SiO_2 greatly enhanced the conversion of ethane and influenced the product distribution. The highest rate and selectivity for acetaldehyde formation was found on a K_2MoO_4/SiO_2 catalyst.

Keywords: Ethane oxidation, acetaldehyde production, oxidation with dinitrogen oxide, silica supported molybdenum oxide catalyst, alkali metal promotors, potassium molybdate catalyst

1. Introduction

The selective oxidation of alkanes is one of the most important catalytic reactions for the production of valuable oxygenated compounds. The yields of these compounds depend sensitively on the nature of the oxidant and also on the composition of the catalyst. As regards the oxidation of ethane, higher yields of partial oxidation products were achieved when N_2O was used instead of O_2 [1–6]. The performance of the various catalysts was influenced by the nature of the support, and by the presence of a small amount of alkali metal salt [5,6]. The effects of such alkali metal additives depend sensitively on their state and on the mode of preparation of the promoted catalyst. An interesting type of promoted catalyst is produced when the promotor and the catalyst form a compound which in most cases exhibits a different structure and a different reactivity. The advantage of this approach is the intimate contact between the promotor ions and the catalyst. Such a contact is virtually impossible to ensure by any method involving their deposition on the large area of support material.

Recently, we found that the use of KVO_3 on a silica support produced a catalyst that was more active, selective and stable in the partial oxidation of ethane than the potassium-free or potassium-promoted V_2O_5/SiO_2 catalyst [5,7]. The primary aim of the present work was to examine whether the use of K_2MoO_4

catalyst leads to any advantageous features in the oxidation of ethane as compared to the use of pure or alkali metal-promoted MoO_3 catalysts.

2. Experimental

The oxidation of ethane was carried out in a fixed-bed continuous flow reactor. The reactor consisted of a quartz tube (20 mm i.d. × 130 mm) which was connected to a capillary tube (2 mm i.d.) so that the products could be rapidly removed from the heated zone. Generally, 0.7–0.8 g of sample was used as catalyst. The reacting gas mixture consisted of 20% of ethane, 40% of the oxidant N_2O, and He as diluent. The flow rate of the reactant was 50 ml/min. Analyses of the exit gases were performed with a Hewlett-Packard 5750 gas chromatograph.

The catalysts were prepared by impregnation of a silica support (Cab-O-Sil) with a basic solution of ammonium paramolybdate or K_2MoO_4 to yield a nominal 2 wt.% of MoO_3. When the catalyst was promoted with potassium, a solution of a potassium compound (K_2SO_4, KNO_2 or KOH) was added to the solution of ammonium paramolybdate before impregnation. The ratio of the K ion to the Mo ion was the same as in the case of K_2MoO_4. K_2MoO_4 was prepared by the method of Retgers [8]. After impregnation the catalysts were dried and calcined in air at 870 K for 5 hours.

For characterization of the catalysts, we determined the BET areas, the number of acidic sites of the samples, and their reducibility. Some of the data relating to the above-mentioned measurements are listed in table 1.

The BET surface area of K containing MoO_3/SiO_2 is greatly decreased except the K_2SO_4-promoted sample. As no such change was observed for KOH-doped or KNO_2-doped, but MoO_3-free SiO_2, it seems likely that solid-phase reactions occurred in the samples, producing different polymolybdates or heteropolymolybdates [9–13]. This was manifested in the reducibility of the catalysts (fig. 1). Whereas the temperature-programmed reduction of MoO_3/SiO_2 started at 770 K, the reduction of all other samples, again with the exception of K_2SO_4-doped catalyst, was observed even at 630 K.

3. Results and discussion

The oxidation of ethane on MoO_3/SiO_2 catalyst occurred at 823 K. In harmony with the results of previous investigations [2,3,5,6], acetaldehyde, ethylene, CO and CO_2 were the main products. Small amounts of CH_4 and C_3 hydrocarbons and traces of C_2H_5OH were also detected. The initial conversion of ethane was about 4–4.5%. The conversion and the rates of product formation slowly decreased in time (fig. 2). A steady state activity was attained only after

Table 1

Some characteristic data of ethane oxidation on silica supported catalysts at 823 K

Catalysts	B.E.T. area (m^2/g)	Number of acidic sites [a] ($\mu mol/g$)	C_2H_6 consumption ($\mu mol/m^2 \cdot s$)		CH_3CHO formation after 250 min		Selectivity (%) after 250 min					
			after 10 min	after 250 min	$\mu mol/g \cdot s$	$\mu mol/m^2 \cdot s$	CH_3CHO	C_2H_4	CH_4	CO	CO_2	C_2H_5OH
MoO_3/SiO_2	166	360.1	$2 \cdot 10^{-3}$	$6 \cdot 10^{-4}$	0.02	$1 \cdot 10^{-4}$	21	31	0	12	36	traces
$(MoO_3-K_2SO_4)/SiO_2$	174	440.5	$3 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	0.01	$6 \cdot 10^{-5}$	2	48	2	6	39	3
$(MoO_3+KOH)/SiO_2$	71	190.6	$1.2 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	0.11	$1.5 \cdot 10^{-3}$	16	23	4	18	38	1
$(MoO_3-KNO_2)/SiO_2$	62	148.8	$1.9 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$	0.06	$1 \cdot 10^{-3}$	6	51	4	13	23	3
K_2MoO_4/SiO_2	28	139.5	$2.1 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	0.12	$4 \cdot 10^{-3}$	27	9	4	26	32	2

[a] The number of acidic sites has been determined by n-butylamine titration.

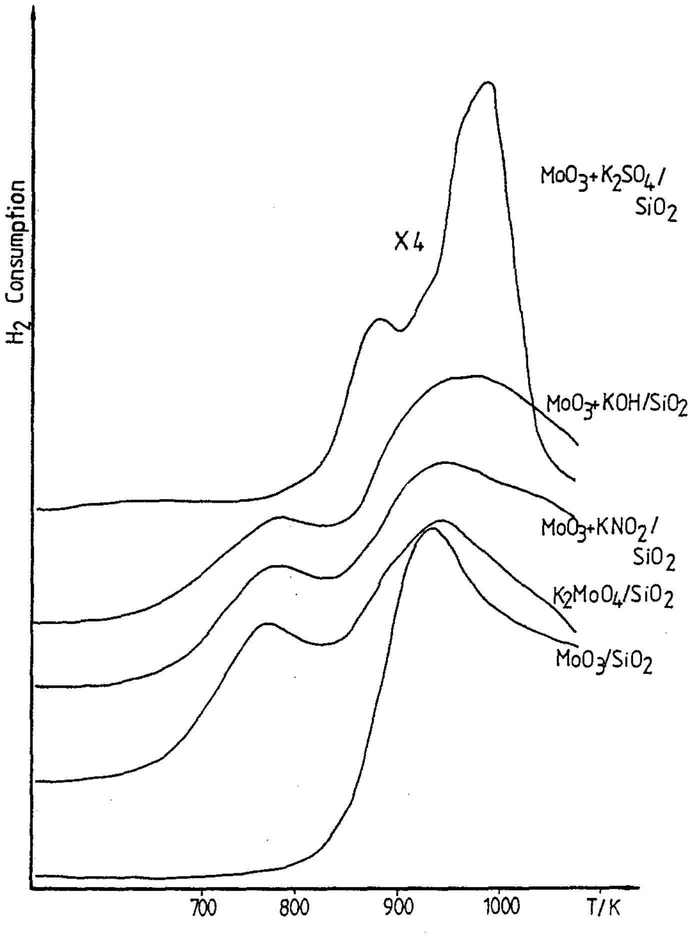

Fig. 1. Temperature-programmed reduction of different catalysts. Heating rate was 40 K min^{-1}, the flow rate of $N_2(90\%)+H_2(10\%)$ was 40 ml min^{-1}. The amount of catalysts was 0.3 g.

several hours. At this stage, the conversion of ethane was about 1%, the selectivity of acetaldehyde formation was about 21% and the selectivity of ethylene formation was higher, at 31%. The overall selectivity for acetaldehyde and ethylene was less than that reported by Mendelovici and Lunsford [3] (they used 1.65 g of catalyst and the flow rate of the reactant was 45 ml/min), which is probably due to the lower space velocity used in the present work.

The addition of the various potassium compounds to the MoO_3/SiO_2 greatly enhanced the conversion of ethane (fig. 2). The marked increase in the activity can not be attributed to a change in the surface area of the catalyst, as the addition of KOH or KNO_2 to MoO_3 significantly lowered the BET area of the MoO_3/SiO_2 sample (table 1).

The potassium compound additives influenced the product distribution of ethane oxidation: the selectivity of acetaldehyde production decreased, while that

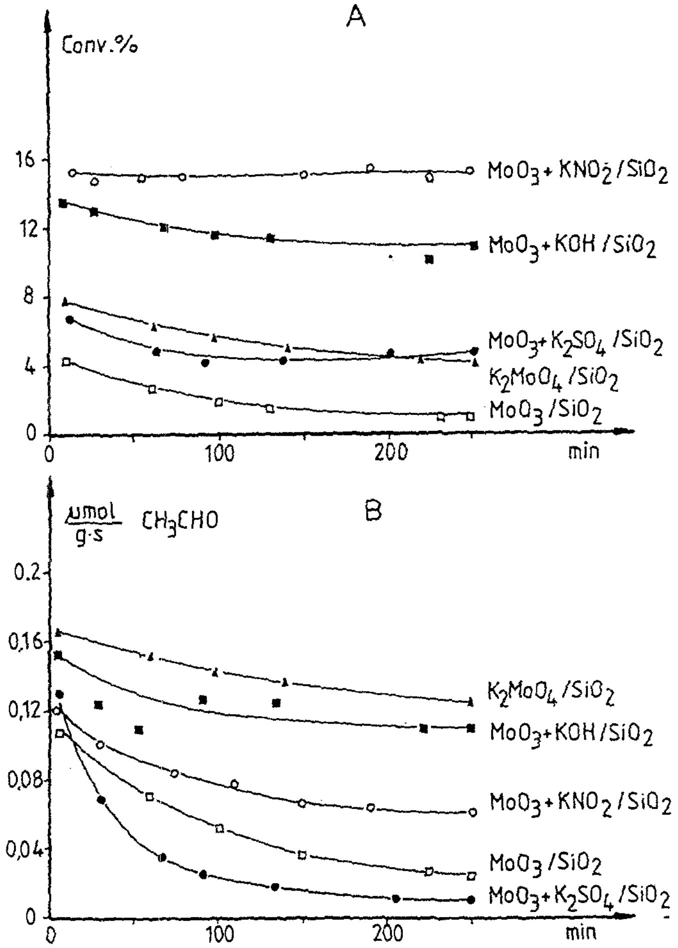

Fig. 2. Conversion of ethane (A) and rate of acetaldehyde formation (B) on different catalysts at 823 K.

of ethylene formation (with the exception of KOH-doped samples) increased (table 1). A small amount of methane (2–4%) was also produced on the K-promoted catalysts. This behaviour is in contrast with the characteristics of V_2O_5 catalysts, where the addition of the same potassium compounds increased the rate of acetaldehyde production by a factor of almost 6–7 [5,7].

Different features were observed for the supported potassium molybdate (K_2MoO_4/SiO_2) catalyst. In this case we obtained the highest initial specific rate for ethane oxidation (taking into account the BET areas), and the highest rate and selectivity of acetaldehyde formation (table 1). In contrast, the production of ethylene was the lowest.

Variation of the contact time on K_2MoO_4/SiO_2 showed that a higher selectivity for acetaldehyde production could be attained at higher space velocities. An increase in this parameter by a factor of 3 by increasing the flow rate from 25 ml/min to 75 ml/min (the amount of catalyst was 0.69 g) enhanced the selectivity of acetaldehyde formation from 12% to 28% and decreased the conversion from 6% to 2.8%. This feature was the same when the amount of the catalyst was varied. This result clearly indicates the occurrence of secondary reactions of acetaldehyde, particularly at high contact times. The space velocity change did not influence the selectivity of ethylene formation.

The effects of the reactant concentrations were determined on a K_2MoO_4 sample pretreated with the reactant gas mixture at 823 K. With increase of the C_2H_6 concentration from 5% to 20%, the CH_3CHO production increased and the CO_2 formation decreased, but no change occurred in the production of ethylene. When the N_2O concentration was increased from 10% to 60%, the conversion of ethane and the selectivities of ethylene and acetaldehyde formation decreased, but the selectivity of CO_2 formation increased.

In conclusion, we can state that the addition of potassium compounds to MoO_3 greatly increased the rate of ethane oxidation; this is most probably connected with the enhanced formation and reactivity of $Mo^{6+}–O^-$ sites which play an important role in the oxidation [3,14]. The species $Mo^{6+}–O^-$ can be formed in the reaction of N_2O with reduced centers Mo^{5+}, the formation of which is facilitated in the presence of alkali metal salts (fig. 1). Additionally, it is necessary to take into account the occurrence of solid-state reactions in MoO_3/SiO_2, producing various oxometalate species, such as polymolybdates, paramolybdates, molybdosilicic acid, etc. [9–13]; the molybdosilicic acid exhibited high activity in the oxidation of methane [10]. However, at high calcination temperatures these species were destroyed and the activity of the catalyst decayed [10]. As the alkali metal compounds possesses higher thermal stabilities, this feature may also contribute to the favourable influence of the promotion with alkali metal salts.

As regards the product distribution, the K_2MoO_4 catalyst exhibited striking behaviour, which differed from that of the alkali-doped and undoped MoO_3 samples, as it promoted mainly the formation of acetaldehyde. This means that on K_2MoO_4 the reaction

$$2Mo^{6+} + C_2H_5–O^- + OH^- = CH_3CHO + H_2O + 2Mo^{5+}$$

is favoured (very probably due to less numbers of acidic sites) as compared to the reaction

$$C_2H_5–O^- = C_2H_4 + OH^-$$

which yields ethylene and requires acidic sites [15].

Finally, it should be mentioned that the partial oxidation of ethane are being investigated on other alkali metal molybdates, too. All of them are to be active catalysts in this oxidation, and the activities and the selectivities exhibit a greater variation with the nature of the cations.

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