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AMMOXIDATION OF TOLUENE OVER MOLYBDENUM OXIDES

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The ammoxidation of toluene was studied both in presence and absence of gaseous oxygen over MoO_3 and in situ prepared Mo_4O_{11} (orth.) and MoO_2. Irrespective of the partial pressure of oxygen, total reaction rates decrease in the following order: $MoO_3 > Mo_4O_{11} > MoO_2$. The corresponding sequence for the selectivity towards formation of benzonitrile was found to depend on the partial pressure of oxygen. In two phase samples, no synergistic effects were observed for the formations of nitrile and carbon oxides. A comparison of rates for selective and nonselective products obtained in presence of gaseous oxygen with those obtained in its absence yield information as to whether the various products are formed at identical or different crystal faces. In the case of MoO_3, nitrile and carbon oxides were found to be competitively formed at the same faces, while over MoO_2 they are formed at different faces. Both options seem to prevail on Mo_4O_{11}.

1. Introduction

Molybdenum is widely used as a component in oxide catalysts for reactions such as hydrogenation, oxidative dehydrogenation, dehydration and selective oxidation [1]. In the selective oxidation and ammoxidation of propylene, molybdenum is used in the form of bismuth molybdates [2]. It is superior to pure MoO_3 for this reaction. The latter has a low activity [3,4]. Nevertheless, MoO_3 has recently been extensively investigated in the oxidation of propylene [5–9], butenes [10], and the ammoxidation of toluene [11] in order to elucidate the role of various crystal faces for selective and non-selective reactions. In the ammoxidation of toluene we found, that both for the formation of benzonitrile and carbon oxides the terminations in the *c*-direction are more active than {100} and {010} faces [11]. One of the objects of the present investigation is to show that on the basis of a comparison of rates for formation of nitrile and carbon oxides obtained in the ammoxidation of toluene in presence and absence of gaseous oxygen, respectively, it can be concluded whether these products are formed on the same crystal faces or not. Results on MoO_3, Mo_4O_{11} (orthorhombic) and MoO_2 are reported.

In oxidation and ammoxidation of hydrocarbons on oxide catalysts, surface lattice oxygen species are consumed in the formation of products. The catalyst surface is then reoxidized using gaseous oxygen [3,12]. As a result of such a mechanism, the catalyst composition depends on reaction temperature and partial pressures of reactants. It can also vary with time-on-stream until steady state is reached [13–16]. Another object of the present investigation is to compare the activities and selectivities obtained over MoO_3 with those obtained over in-situ prepared Mo_4O_{11} and MoO_2, and also to observe if there is in two phase samples any synergetic effects, or effects due to defect formation. Such effects have been observed for two phase vanadium oxide catalysts [13,15]. In the case of MoO_3, if mixed with e.g. Sb_2O_4 or $BiPO_4$, synergetic effects have been reported in the selective oxidation of isobutene [17].

2. Experimental

The catalytic experiments were carried out at atmospheric pressure using a differential plug flow reactor made of glass and with an internal diameter of 6 mm. Ammoxidation of toluene was investigated both in the presence and absence of gaseous oxygen. The total inlet flow was in all cases 114 standard cm^3/min. In the experiments with gaseous oxygen the composition of the reactant stream was N_2 87.8 vol%, O_2 8.78 vol%, NH_3 2.63 vol%, and toluene 0.78 vol%. When no gaseous oxygen was fed, the concentrations of N_2, NH_3 and toluene were 96.58 vol%, 2.63 vol% and 0.78 vol%, respectively. The reaction temperature was 455 °C. Total conversions did not exceed 10%, and were in most cases below 3%. The outlet stream was analyzed on a Varian Vista 6000 gas chromatograph, using an arrangement of columns as described elsewhere [11].

The MoO_3 sample was obtained by sublimation of the powdered chemical (Mallinckrodt, analytical reagent) in a stream of air. After sieving, a relatively uniform sample was obtained, which was then used in the experiments. Samples containing reduced oxides were prepared in-situ according to fig. 1.

MoO_3 (60 mg) was run in ammoxidation with $O_2(g)$. Steady state was reached almost immediately and reaction rates were measured. The reaction was then continued without $O_2(g)$, causing a reduction of the sample. Reaction rates were measured as a function of time on stream. Values obtained after 25 minutes were for a sample composed of both MoO_3 and MoO_2. Then $O_2(g)$ was added to the inlet stream, rates were measured immediately and again after 63 minutes, now over a sample which had been oxidized to a mixture of MoO_3 and Mo_4O_{11}. A flow without $O_2(g)$ was introduced and rates were immediately measured.

After MoO_3 had been used for 108 minutes in absence of $O_2(g)$, the rates measured were for a sample consisting of almost pure MoO_2. Oxygen was then introduced, rates were measured both immediately and again after 78 minutes, now for an almost pure Mo_4O_{11} sample. The flow was changed without $O_2(g)$.

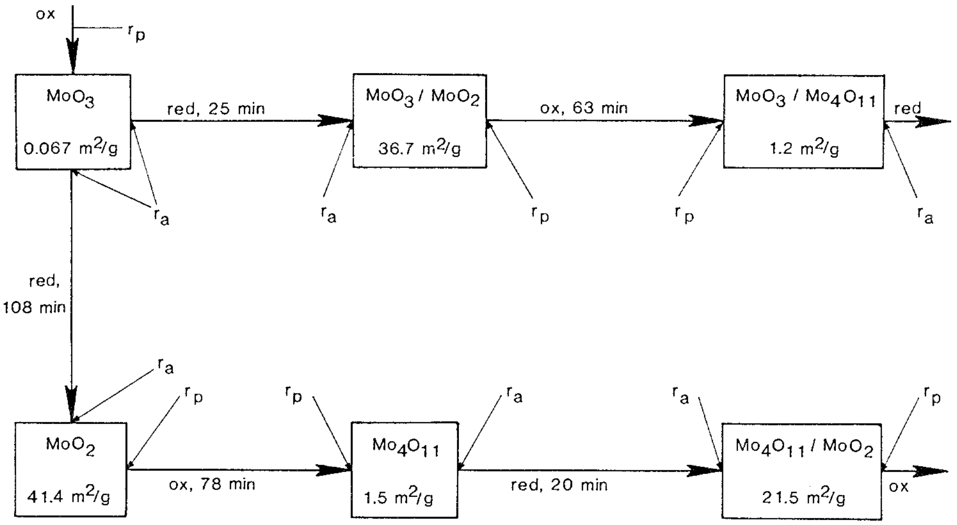

Fig. 1. In situ preparation of molybdenum oxides by the use of ammoxidation of toluene in presence (ox) and absence (red) of O_2(g). Specific surface areas are given, and r_a and r_p indicate rate measurements in absence and presence of O_2(g), respectively.

Reaction rates were measured immediately, thus valid for Mo_4O_{11}, and after 20 minutes, representative for a sample with both Mo_4O_{11} and MoO_2. For the latter sample, a flow with O_2(g) was now introduced and rates were immediately measured. This procedure allowed rates to be measured for all samples both in presence and absence of O_2(g). Before making activity mesurements, the whole procedure was run step-wise to allow for analyses of phase compositions and surface area determinations.

X-ray powder diffractographs were obtained with a Guinier-Hägg camera using CuK_{α_1} radiation. The interplanar spacings were determined, and the phases present were identified by comparison with the references in the JCPDS file [18]. The specific surface areas of the samples, which are given in fig. 1, were determined with a gravimetric BET apparatus.

The solid state phenomena occuring in the above treatments were found to be reproducible and have recently been described in detail [19]. The two-phase samples contained approximately equal amounts of both phases, however, the particle sizes decreased with increased degree of reduction.

3. Results and discussion

Specific reaction rates and selectivities for the formation of benzonitrile, benzene, CO_2 and CO obtained in the presence of gaseous oxygen are given in table 1. A comparison of the results obtained over the single oxide samples shows that for all products the rates decrease as follows: $MoO_2 > Mo_4O_{11} > MoO_2$. The

Table 1

Rates (moles/h, m^2) and selectivities (%) for the formation of products in the ammoxidation of toluene in the presence of gaseous oxygen

Sample	C_6H_5CN		C_6H_6		CO_2		CO	
	Rate	Sel.	Rate	Sel.	Rate	Sel.	Rate	Sel.
MoO_3	1.35×10^{-3}	68.8	7.95×10^{-5}	4.1	4.74×10^{-4}	24.1	5.95×10^{-5}	3.0
Mo_4O_{11}	3.47×10^{-4}	76.2	4.53×10^{-7}	0.1	1.01×10^{-4}	22.3	6.40×10^{-6}	1.4
MoO_2	6.72×10^{-6}	50.1	2.83×10^{-8}	0.2	5.53×10^{-6}	41.2	1.13×10^{-6}	8.5
MoO_3/Mo_4O_{11}	4.17×10^{-4}	73.7	-	-	1.31×10^{-4}	23.1	1.82×10^{-5}	3.2
MoO_3/MoO_2	1.90×10^{-5}	61.6	-	-	1.03×10^{-5}	33.4	1.53×10^{-6}	5.0
Mo_4O_{11}/MoO_2	4.39×10^{-5}	63.2	-	-	2.25×10^{-5}	32.4	3.06×10^{-6}	4.4

selectivity for formation of benzonitrile is found to follow the sequence: $Mo_4O_{11} > MoO_3 > MoO_2$, while the reverse sequence is observed for the formation of carbon oxides. In the ammoxidation in absence of gaseous oxygen, table 2, the same activity relationship exists, i.e. $MoO_3 > Mo_4O_{11} > MoO_2$. The selectivity for formation of nitrile is high for all samples but a sequence can be distinguished as follows: $MoO_2 > MoO_3 > Mo_4O_{11}$.

Thus, it can be concluded that the total reaction rate over molybdenum oxides, irrespective of the partial pressure of oxygen diminishes when the valence of the cation decreases. This is, however, not a general rule. In studies [13,15] of a similar reaction, the ammoxidation of 3-methylpyridine, over vanadium oxides, it was found that V_6O_{13} and VO_2(B) are more active than V_2O_5, while V_4O_9 and VO_2(tetragonal) have lower activities. These results show that catalytic activity is primarily not related to the cation valence but to the geometrical arrangement of surface atoms. Also in support of this conclusion is the finding that the selectivity sequence for the formation of benzonitrile over molybdenum oxides is highly dependent on the partial pressure of oxygen, which is a crucial factor governing surface structure [16].

Considering tables 1 and 2, it can be concluded that for the formations of nitrile and carbon oxides, the activity and selectivity measured over mixed oxide samples generally fall within the limits given by the values obtained for the constituent oxides. Therefore, in these cases, there are no evidence of any so-called synergetic effect. Such an effect would exist if data for a mixed oxide sample cannot be treated as a combination of data obtained over pure oxides. This may be the case for the formation of benzene in the absence of gaseous oxygen over MoO_3/Mo_4O_{11} and Mo_4O_{11}/MoO_2 samples, where rates and selectivities are higher than those measured over the constituent oxides.

In the ammoxidation of 3-methylpyridine over mixed vanadium oxide samples, synergetic effects has been reported for the formation of nitrile and CO_2 over V_2O_5/V_6O_{13} [13] and VO_2(B)/VO_2 (tetragonal) [15] samples. In both of these samples the synergy has been related to amorphous defects, formed under the

Table 2
Rates (moles/h, m^2) and selectivities (%) for the formation of products in the ammoxidation of toluene in the absence of gaseous oxygen

Sample	C_6H_5CN		C_6H_6		CO_2		CO	
	Rate	Sel.	Rate	Sel.	Rate	Sel.	Rate	Sel.
MoO_3	3.03×10^{-3}	92.7	1.94×10^{-6}	0.1	2.19×10^{-4}	6.7	2.09×10^{-5}	0.6
Mo_4O_{11}	4.37×10^{-4}	89.7	4.97×10^{-7}	0.1	4.61×10^{-5}	9.5	3.65×10^{-6}	0.7
MoO_2	7.22×10^{-6}	94.6	8.45×10^{-8}	1.1	2.32×10^{-7}	3.0	9.69×10^{-8}	1.3
MoO_3/Mo_4O_{11}	5.98×10^{-4}	88.8	1.55×10^{-5}	2.3	5.25×10^{-5}	7.8	7.30×10^{-6}	1.1
MoO_3/MoO_2	2.34×10^{-5}	94.0	1.12×10^{-7}	0.4	1.29×10^{-6}	5.2	8.72×10^{-8}	0.4
Mo_4O_{11}/MoO_2	6.53×10^{-5}	92.6	3.06×10^{-6}	4.3	1.58×10^{-6}	2.3	5.59×10^{-7}	0.8

influence of the reaction medium [14,15]. These types of defects were only observed in the two phase molybdenum oxide samples due to electron beam damage [19,20]. At present no explanation can be offered on the origin of the synergetic effect observed in the case of benzene formation.

It is generally accepted that in oxidation of hydrocarbons electrophilic oxygen species, O^- and O_2^-, participate in the formation of degradation products finally leading to the formation of carbon oxides, while nucleophilic oxygen species, O^{2-}, are inserted into intermediates of selective oxidation routes [11,12,16,21]. Usually, catalysts for selective oxidation can also be used in the ammoxidation of the same compound producing nitrile. The reason is that some of the nucleophilic oxygen species react with ammonia giving =NH species, which can then be inserted into the reactive hydrocarbon intermediate [2,11,22]. Due to the fact, that electrophilic oxygen species lack electrons they are weaker bonded to the surface as compared with nucleophilic oxygen species. Consequently, in an atmosphere without gaseous oxygen the ratio of electrophilic to nucleophilic oxygen species at the surface will be less than the same ratio prevailing in presence of molecular oxygen. This fact can be used to ascertain whether selective and nonselective oxidation occur at the same crystal face or at different faces. Thus, if initial rates in presence and absence of gaseous oxygen are compared, two different patterns of behaviour are possible:

(i) If carbon oxides and selective product are formed at different faces, then we should expect initial rates for combustion products to decrease when the reactant feed is depleted from gaseous oxygen. Initially, the rate for formation of selective product will hardly be affected.

(ii) If carbon oxides and selective product are formed at the same faces, then a depletion of the feed of gaseous oxygen, also should result in a decrease of the rates for combustion products. However, in this case, the rate for formation of selective product should increase initially due to the fact that the concentration of adsorption sites (naked cations) increases, the concentration of nucleophilic oxygen species is almost unchanged and that the competitive degradation occurring at the same face is reduced.

Comparison of rates in the presence and absence of gaseous oxygen shows that, for MoO_3, the rate for nitrile formation is more than a factor 2 higher in absence of gaseous oxygen. Simultaneously, the rates for formation of carbon oxides decrease approximately by the same factor. In the case of MoO_2, the same type of comparison shows that the rate for nitrile formation is not significantly affected by a decrease in oxygen pressure, but that the rates for carbon oxides formations strongly diminish (10–20 times). Considering Mo_4O_{11}, it is seen that in absence of gaseous oxygen the rate for nitrile formation is about 25% higher compared with the value obtained in its presence. At the same time, the rates for formation of carbon oxides is reduced to half. From these observations, it can be concluded that on MoO_3 both nitrile and carbon oxides are competitively formed at the same faces. Over MoO_2 it is obvious that selective and nonselective products are formed at different types of faces. The situation on Mo_4O_{11} is more complex, but it is not unlikely that there exist faces at which nitrile and carbon oxides formations competitively occur, as well as some planes at which only one type of reaction takes place.

In a previous study of the reaction between toluene and ammonia over MoO_3 crystal samples with different distributions of surface plane, we found that considerable amounts of produced nitrile and carbon oxides could be related to the terminations in the *c*-direction, i.e. $\{001\}$ and $\{h01\}$ faces [11]. This finding that nitrile and carbon oxides are competitively formed at the same faces is confirmed by the results of the present investigation. This type of comparison may be of general applicability in studies of structure sensitivity over metal oxide catalysts in (amm)oxidation reactions.

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