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EFFECT OF IRON ON THE BEHAVIOR OF Fe_2O_3-MoO_3/SiO_2 AMMOXIDATION CATALYSTS

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Catalytic ammoxidation of propylene was studied using Fe_2O_3-MoO_3/SiO_2 catalysts, which have been prepared following a special method. Interaction of ammonia with the catalysts was studied by means of IR spectroscopy and gravimetrically using a McBain balance. Introduction of iron into MoO_3/SiO_2 catalysts modifies acidic as well as redox properties.

Катализаторы Fe_2O_3-MoO_3/SiO_2 были приготовлены специальными методами. Их каталитические свойства исследовали в аммоксидировании пропилена. Взаимодействие аммиака с катализаторами было исследовано с помощью ИК-спектроскопии и балланса МакБэйна. Взаимодействие железа с катализаторами MoO_3/SiO_2 изменяет как кислотные, так и редокс свойства катализаторов.

It is well known that most industrial catalysts for the production of acrylonitrile contain either $Fe_2(MoO_4)_3$ or the so called X-phase Bi_3FeMoO_{12}. Pure $Fe_2(MoO_4)_3$ (a very good and often investigated catalyst for methanol oxidation [1]), however, is quite inactive in the ammoxidation of propylene, as has been shown by us several years ago [2].

It has been shown further [3] that with Bi_2O_3-MoO_3/SiO_2

catalysts the formation of "destructive" ammoxidation products like acetonitrile and prussic acid decreases as contents of bismuth is increased. It was assumed that the introduction of Bi_2O_3 into the catalytic system gives rise to the formation of Bi-O-Mo-bonds thus increasing the electronic density of the molybdenum ion and simultaneously decreasing the number of both Brönsted and Lewis centers on the surface.

The objective of the present work is the influence of iron present in the MoO_3/SiO_2 system on the ammoxidation of propylene.

EXPERIMENTAL

To prepare the catalysts, a special method of impregnation has been used, by which a high dispersity of the active phase is ensured [3,4]. The first step is the preparation of a MoO_3/SiO_2 sample (containing 3.7 wt.% of Mo), which was calcined at 350 °C and than divided into three parts. One of them was used as a reference sample throughout all further investigations. The other parts were impregnated with quantities of $Fe(NO_3)_3$ corresponding to 0.32 or 1.27 wt.% of Fe, respectively, and calcined at 450 °C in air.

Catalytic investigation was carried out at 450 °C in a fluid bed reactor using a gas mixture of propylene : air : ammonia (ratio 1:10:1) with a flow rate of 14.4 dm^3/h and 40 cm^3 of catalyst (Table 1 and 2).

IR spectra were recorded by a UR 20 IR spectrophotometer of VEB Carl Zeiss Jena equipped with a vacuum cell. Pretreatment of self-supporting discs was carried out as described [3]. Results of IR spectroscopy and adsorption studies are presented in Table 3. Initial reduction rate was determined in a pulse reactor by means of 1 cm^3 pulses of hydrogen in an argon flow using 1 g of catalyst (Fig. 1).

RESULTS AND DISCUSSION

As can be seen from Tables 1 and 2, addition of iron increases the amount of CO_2 and HCN. On the other hand rate and selectivity of acetonitrile formation significantly decrease,

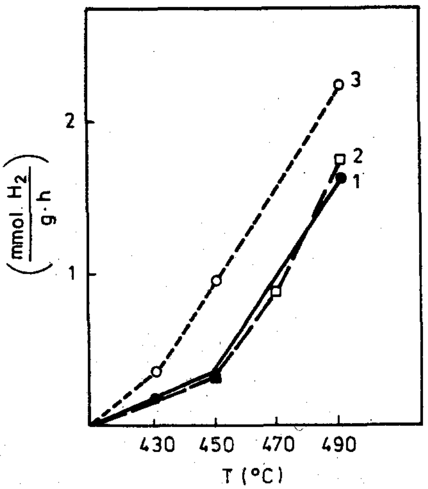

Fig. 1. Initial reduction rate in dependence on temperature

1- 3.7 wt.% Mo (I)
2- (I) + 0.32 wt.% Fe
3- (I) + 1.27 wt.% Fe

Table 1

Ammoxidation of propylene on Fe_2O_3-MoO_3/SiO_2 catalysts calcined for 1 h at 450 °C in air at 430 °C

Contents (wt.%) Mo	Fe	Overall rate	Reaction rate (mol/h) Partial rate of product formation CH_2CHCN	CH_3CN	HCN	CO_2
4.7	0	1.7	0.47	0.96	0.22	0
4.7	0.4	1.6	0.47	0.49	0.37	0.25
4.7	1.6	1.9	0.49	0.33	0.60	0.44

whereas formation of acrylonitrile is not influenced. Investigation of analogous catalysts by means of Mössbauer and ESR spectroscopy [5] shows that iron after impregnation and calcination at 100 °C forms iron oxide. Calcination at 400 °C

Table 2

Selectivity of product formation on Fe_2O_3-MoO_3/SiO_2 and Bi_2O_3-MoO_3/SiO_2 catalysts calcined for 1 h at 450 °C in air at 430 °C

Contents (wt.%)			Selectivity (%)				
Mo	Fe	Bi	CH_2CHCN	CH_3CN	HCN	CO_2	CO
4.7	0	0	29	58	13	0	0
4.7	0.4	0	30	31	24	15	0
4.7	1.6	0	26	18	33	23	0
4.0	0	0	12	58	15	4	3
4.0	0	3.5	11	48	16	5	3
4.0	0	7.0	15	41	17	8	5
4.0	0	14.0	34	15	15	9	9

leads to the formation of a structure similar to $Fe_2(MoO_4)_3$, i.e. an interaction between iron and molybdenum took place.

Comparing the effect of the addition of iron and bismuth (Table 2) some differences in selectivity of the formation of prussic acid and CO_2 can be seen. Whereas addition of bismuth does not affect significantly the selectivity of the formation of these products, addition of iron increases both the formation of HCN and CO_2. Therefore, we can conclude that the increase of the amount of HCN and CO_2 results from the addition of iron.

Table 3 shows that addition and increasing contents of iron decreases the overall acidity, which can be seen both from the decrease of the total amount of adsorbed ammonia and from the decrease of the formation of NH_4^+ ions on Brönstead centers (1440 cm^{-1} band). In detail, already the addition of small amounts of iron (Mo:Fe ratio was about 7) results in a great change of acidity; a change of the ratio of intensities of the IR bands at 1440 and 1630 cm^{-1} which shows the decreasing role of Brönstead acidity was additionally observed. A further increase of the iron contents gives only an insignificant change

Table 3

Ammonia adsorption on Fe_2O_3-MoO_3/SiO_2 catalysts (3.7 wt.% Mo)

Iron contents (wt.%)	Pretreatment	Absorbance (corrected for 20 mg disc)		m_1	m_2	$\frac{a_1}{a_2}$
		1440 cm^{-1}	1630 cm^{-1}	(mmol/g)		
0	NH_3	-	-	1.03	-	-
	vacuum	0.22	0.05	0.84	0.48	4
	H_2O, NH_3, vacuum	0.36	0.01	-	0.48	36
	373 K	0.28	0.01	-	0.37	28
0.3	NH_3	-	-	1.05	-	-
	vacuum	0.12	0.05	0.56	0.30	2
	H_2O, NH_3, vacuum	0.20	0.03	-	0.34	7
	373 K	0.11	0.01	0.07	0.18	11
	693 K, O_2, NH_3, vacuum	0.11	0.06	-	0.34	2
	H_2O, NH_3, vacuum	0.16	0.03	-	0.33	5
	373 K	0.06	0.01	-	0.14	6
1.3	NH_3	-	-	0.97	-	-
	vacuum	0.13	0.06	0.47	0.40	2
	H_2O, NH_3, vacuum	0.19	0.03	-	0.36	6
	373 K	0.10	0.02	0.19	0.19	5
	693 K, O_2, NH_3	-	-	0.80	-	-
	vacuum	0.11	0.07	0.30	0.40	2
	H_2O, NH_3, vacuum	0.19	0.04	-	0.38	5
	373 K	0.09	0.03	0.19	0.22	3

Pretreatment: H_2O - 2.0 kPa, NH_3 - 2.7 kPa, vacuum - 0.1-1 Pa

m_1 - NH_3 adsorption from McBain balance (mmol/g)

m_2 - NH_3 adsorption from IR spectra according to [4] (mmol/g)

$\frac{a_1}{a_2}$ - absorbance ratio $\frac{A_{1440\ cm^{-1}}}{A_{1630\ cm^{-1}}}$

of acidity. Raising the temperature of calcination from 350 °C to 420 °C the decrease of the ratio between the intensities of both bands continues. This indicates that the number of Lewis sites increases at the expense of the Brönstead sites.

Figure 1 shows the initial rates of reduction of the catalysts. It can be seen that increasing iron contents increase the reduction rate especially in the region of 430-480 °C. It seems reasonable to conclude that the capability of Fe^{3+} ions to accept electrons strongly influences the properties of these catalysts: at least the stabilization of the Mo^{6+} state and the formation of Lewis centers depend on the Fe^{3+}/Fe^{2+} equilibrium.

Comparison of experimental values shows that the Bi_2O_3-MoO_3/SiO_2 catalyst containing 3.5 wt.% of Bi [3] has a higher acidity than the corresponding Fe_2O_3-MoO_3/SiO_2 catalyst with the same Me:Mo ratio, containing 1.3 wt.% of Fe. In particular it was found that Bi_2O_3-MoO_3/SiO_2 catalysts always contain more Lewis centers than Fe_2O_3 = MoO_3/SiO_2 catalysts, in both cases related to the overall acidity. Both iron and bismuth cause a decrease of products of "destructive" ammoxidation, in the case of Fe especially of CH_3CN. However, the change of redox properties due to the introduction of iron, i.e. the formation of weakly bonded oxygen, favors total oxidation to give HCN and CO_2.

So the results obtained are as follows: - Introduction of iron into MoO_3/SiO_2 catalysts - like introduction of Bi - diminishes overall acidity but simultaneously increases the ratio of Lewis to Brönstead acidity.

- Iron also changes the redox properties of the system strengthening its capability to enhance total oxidation to HCN and CO_2.
- Like bismuth, iron suppresses the formation of products of "destructive" ammoxidation but simultaneously strongly increases the total oxidation.

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