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Characterization of CrAPO-5 Materials in Test Reactions of Conversion of 2-Methyl-3-butyn-2-ol and Isopropanol

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CrAPO-5 materials with various amounts of Cr(III) stably incorporated into the framework positions were tested in the reactions of conversion of 2-methyl-3-butyn-2-ol (MBOH) and isopropanol. The results were compared with those obtained over similar materials containing extraframework chromium species and over nonsubstituted $AlPO_4$-5. The products of the reactions indicated an increased acidity of catalytic sites in CrAPO-5 compared to that in $AlPO_4$-5. The yield of conversion depends mainly on the amount of chromium and its distribution. The multivalent extraframework Cr species yielded similar catalytic effects as framework Cr centers. However, their activity dropped very quickly due both to the hindrances to alcohol molecules in accessing the catalytic sites in the pores clogged by these species and to the faster coking. © 2002 Elsevier Science (USA)

Key Words: **CrAPO-5; isomorphous substitution of Cr; conversion of methylbutynol; conversion of isopropanol; activity of framework Cr.**

INTRODUCTION

Catalytic properties of chromium, especially in the redox reactions, evoked high interest in the molecular sieves containing Cr. These materials were expected to reveal favorable catalytic properties (1) in relation to oxides or homogeneous catalysts in the form of solutions, due to creation of separated and well-distributed catalytic centers. Additionally, such heterogeneous crystalline solids might offer easier managing in the catalytic processes.

Substitution of Cr into aluminophosphate molecular sieves of $AlPO_4$-5 (AFI structure type) has long been tried (2–15). Catalytic activity of Cr-containing $AlPO_4$-5 materials has been reported in numerous papers (e.g., 6–10). However, all these contributions have either given no evidence for framework incorporation of Cr or concluded that chromium was not located in framework positions (e.g., 10–12). A stable incorporation of higher amounts of Cr into the framework of $AlPO_4$-5 has appeared to be possible under significantly modified conditions of synthesis (16–20) and can be best achieved with use of cotemplates (18–20). These materials have extensively been characterized. The structure has been determined from X-ray diffraction patterns (XRD) (16, 19), crystal dimensions and morphology from scanning electron microscopy (SEM) (16, 19, 20), and sorption properties and accessibility to the pores from adsorption measurements for nitrogen, water, and benzene (16, 17, 19), as well as from fluorescence investigations (19), amount of Cr from chemical analysis (ICP) (16–20), state and stability of chromium in the crystals from electron paramagnetic resonance (EPR) (18), UV–vis spectroscopy (16, 19), nuclear magnetic resonance (^{27}Al and ^{31}P MAS NMR) (19), thermogravimetric analyses (TG, DTG, DSC) (19), ion exchange tests (19), and leaching tests (19). All these techniques have indicated a stable incorporation of the Cr^{3+} ions into framework positions for Al^{3+}. Chromium is fourfold bonded to the framework atoms and its coordination is complemented by two additional ligands (water after calcination) to the distorted octahedral one (19). Given this wide variety of methods, the catalytic tests are the necessary complement for fuller characterization of the CrAPO-5 materials.

Two catalytic reactions were employed to test the behavior of the synthesized CrAPO-5 materials and to obtain information about the nature of the catalytic centers (21–25). The test Reaction 1, conversion of 2-methyl-3-butyn-2-ol (MBOH), was applied to determine the acid–base properties/character of the examined materials.

Conversion of MBOH, the simplest tertiary alkynol, proceeds, depending on the character of catalysts, as shown in Scheme 1. The conversion over acidic catalysts such as ZSM-5 or silica–alumina leads to dehydration, yielding 3-methyl-3-buten-1-yne (MBYNE) with almost 100% selectivity (21–24). In parallel, small quantities of 3-methyl-2-buten-1-al (PRENAL) can be obtained (23, 24). The dehydration activity is then related to the surface acidity. The conversion over solid basic catalysts like magnesium oxide, zinc oxide, or alkali-exchanged X zeolites results only in

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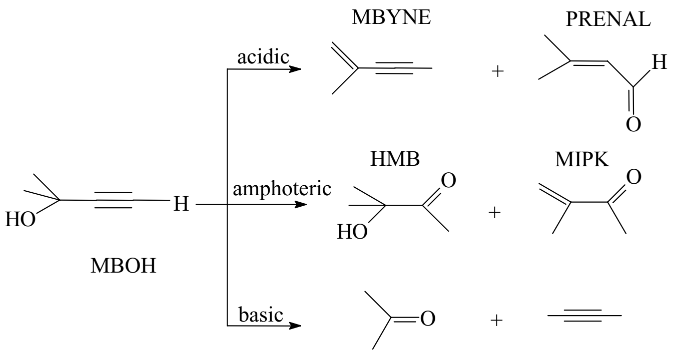
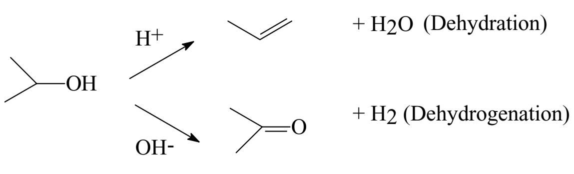


SCHEME 1

acetone and acetylene (22, 23). Over amphoteric catalysts, MBOH yields essentially 3-methyl-3-butene-2-one (MIPK), which can be accompanied by acetone and acetylene at clearly lower selectivities (22). The latter products are formed following the basic mechanism. Over amphoteric ZrO_2, 3-hydroxy-3-methyl-2-butanone (HMB) can be formed with 76% selectivity.

The test Reaction 2 (Scheme 2), conversion of isopropanol (propanol-2), was chosen to confirm the character of catalytic sites in CrAPO-5. The conversion is possible over all acidic sites of any strength and results in dehydration to propene, which is the main product of the reaction (22, 25). A small amount of diisopropylether (DIPE) can also be formed as by-product via intermolecular dehydration of propanol-2 (22, 25). Over basic centers, dehydrogenation of isopropanol to acetone occurs (22). However, basicity of a catalyst can only be revealed when a small amount of a redox component is present (22). With no redox properties, formation of acetone occurs only at a higher temperature, above 573 K (26).

Substitution of Cr^{3+} for Al^{3+} in the framework of $AlPO_4$-5 does not induce an additional framework charge and ion-exchange ability (19). The only result is a compositional heterogeneity which can influence sorption properties of the materials (17). This indicates that the Cr heteroatoms create sorption centers able to interact with molecules adsorbed in the pores. In this light, it was interesting to examine the CrAPO-5 materials in catalytic reactions in order to check the activity and/or character of the chromium centers and to compare the results with those published previously (6–10) for the materials with undefined states of Cr. The aim of the study was to broaden the qualitative characteristics of the new CrAPO-5 materials and their Cr centers. It was especially interesting due to the unusual state of Cr with four framework bonds and two additional ligands, which is unusual for zeolite-like materials. Catalytic behavior and properties of active sites of CrAPO-5 have been characterized in relation to the materials with extraframework Cr species and to nonsubstituted $AlPO_4$-5.



SCHEME 2

EXPERIMENTAL

The CrAPO-5 samples were synthesized as described elsewhere (16–19). The as-prepared crystalline products were calcined at 773 K under air for at least 48 h. The materials were characterized by numerous techniques (cf. Introduction). For details, see Refs. (16–20).

Test Reactions

A fixed-bed reactor was used as the standard method. All catalysts (500 mg) were first activated at 473 K under a nitrogen flow (2.6 L/h) for 2 h. Next, the temperature was increased to 623 or 553 K for the conversion of MBOH or isopropanol, respectively. Then, the reactant stream, preheated in a saturator system, was admitted into the reactor under the N_2 flow (2 and 4 L/h for Reactions 1 and 2, respectively). The effluents were analyzed online with a gas chromatograph after an initial 10 min (0 h in each Table) and then every hour. The same reactions were performed over nonsubstituted $AlPO_4$-5.

RESULTS AND DISCUSSION

The CrAPO-5 crystals were of the form of hexagonal prisms typical of the AFI structure type. Their dimensions as well as the content of Cr are given in Table 1. The structure after calcination (XRD) remained unchanged (16–20).

The CrAPO-5 materials used in the test reactions (Table 1) are divided into two groups: (i) samples 1–4, which show high sorption (HS) capacities for nitrogen and

TABLE 1

Characteristics of the Examined CrAPO-5 and Reference $AlPO_4$-5 Materials

Sample no.	Volume of adsorbed nitrogen (cm^3/g)	Cr content (mmol/g)	u.c./Cr	Dimensions of crystals $(l \times d)^a$ (μm)
1	69.0	0.321	2	10–20 × 40–50
2	76.0	0.157	3.5	10–50 × 10–50
3	76.0	0.135	4	5–50 × 5–60
4	94.0	0.065	10	50–70 × 50–70; 10–20 × 50–60
5	15.0	0.109	5.5	200–400 × 50–60
6	7.0	0.046	14	400 × 30–50
$AlPO_4$-5	67.0	—	—	150–200 × 30–40

[a] l, Length; d, width of the crystals.

TABLE 2

Conversion of MBOH over CrAPO-5 Samples 1–4 (Table 1)

Time (h)	Conversion (%)				Selectivity (%)											
					MBYNE				Acetylene				Acetone			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
0	47.75	33.80	25.28	29.15	53.43	47.54	55.73	71.06	16.82	14.64	16.25	10.14	29.72	37.82	28.02	18.77
1	27.61	19.68	10.14	7.57	33.94	23.05	23.60	43.43	24.07	21.27	28.33	20.64	42.00	55.68	48.06	35.93
2	19.86	17.74	10.92	12.38	26.76	11.69	11.03	15.87	26.72	25.47	32.99	30.58	46.52	62.83	55.97	53.56
3	16.09	20.18	13.29	20.30	21.84	6.87	5.99	6.62	28.59	26.46	34.68	33.99	49.57	66.67	59.31	59.39
4	15.20	22.23	13.97	25.30	13.62	4.47	0	3.06	30.28	27.04	36.64	35.32	56.09	68.49	63.30	61.62
5	14.29		15.63	29.95	6.08		0	0	34.33		36.76	36.59	59.59		63.24	63.41
6			16.26	32.29			0	0			36.78	36.43			63.22	63.57
7			16.89	33.27			0	0			36.87	36.51			63.13	63.49
8			16.94	30.73			0	0			36.66	36.40			63.34	63.60

benzene (16–19), and (ii) samples 5–6, which reveal very low sorption (LS) capacities. The crystals of well-sorbing samples are shorter (*c*-axis, direction of the channels) and exhibit higher contents of Cr. The HS materials contain predominantly the Cr^{3+} ions stably incorporated into framework positions (16–19). These ions cannot undergo redox reactions and their pseudotetrahedral coordination sphere in the framework is complemented by two additional water ligands (in the calcined state), located in the pores, to the favored (pseudo) octahedral one. In the LS materials, chromium occurs mainly as multivalent extraframework species which cause strong clogging of the pores (16–19). In spite of these differences, the catalytic properties of all the CrAPO-5 materials are similar to a high extent (see Tables 2–4 and 5–7 for conversion of MBOH and isopropanol, respectively). These surprising observations are in agreement with the EPR investigations (18), which also did not reveal significant differences between the HS and LS materials.

The conversion of MBOH proceeds with a very low yield of several percent at temperatures below 553 K. The yield starts to increase above 573 K when Cr loses its two water ligands, which is reflected in the reversible change of color (19). For this reason, the experiments were carried out at 623 K. For both groups of the CrAPO-5 materials and for $AlPO_4$-5, three compounds were found among the products of the MBOH conversion, 3-methyl-3-buten-1-yne (MBYNE), acetylene, and acetone, but no PRENAL (Table 2–4). The conversion for both groups of CrAPO-5 was always higher at the beginning of the process; then it decreased significantly after 1 h and was maintained at the same level or slightly increased for the next several hours. $AlPO_4$-5 showed a very rapid decrease in the conversion (Table 4). This decline of the yield over all the CrAPO-5 materials was accompanied by a decrease in selectivity to MBYNE with a simultaneous increase in selectivity to acetylene and acetone. For $AlPO_4$-5, all these values remained constant.

TABLE 3

Conversion of MBOH over CrAPO-5 Samples 5 and 6 (Table 1)

Time (h)	Conversion (%)		Selectivity (%)					
			MBYNE		Acetylene		Acetone	
	5	6	5	6	5	6	5	6
0	54.74	24.44	61.70	67.68	13.99	12.23	24.30	20.07
1	26.30	8.76	42.97	48.23	21.04	18.93	35.99	32.84
2	17.70	7.28	34.91	30.58	24.10	25.67	40.99	43.75
3	14.41	8.36	27.55	17.21	26.66	30.27	45.80	52.51
4	13.70	10.96	21.46	9.53	29.03	33.34	49.51	57.13
5	14.32	14.64	16.69	5.59	30.84	34.70	52.47	59.72
6	15.39	18.41	12.73	0	32.14	36.55	55.14	63.45

As seen in Table 2, the yield of the MBOH conversion follows the Cr content of the catalysts except sample 4. This sample shows the initial conversion between those of catalysts 2 and 3 in spite of a more than two times lower content of Cr. Moreover, the conversion over sample 1 decreases with reaction time to values similar to those for sample 5 (see Table 3), while the conversions over samples 2 and 3 pass a minimum and likely tend to stabilize at higher values. The conversion over sample 4, after passing the minimum, seems to stabilize at values higher even than the initial one. These observations confirm the activity of

TABLE 4

Conversion of MBOH over $AlPO_4$-5 (Table 1)

Time (h)	Conversion (%)	Selectivity (%)		
		MBYNE	Acetylene	Acetone
0	64.40	98.30	0.46	1.24
1	26.09	98.52	0.23	1.26
2	4.57	100.00	0	0

the Cr centers in the conversion process but suggest simultaneously a significant role of another, likely space/steric, factor(s). From this point of view, the changes of the conversion correspond especially well to the values of sorption capacities (Table 1), which illustrate the possibility of diffusion of sorbate molecules into the channels.

The highest selectivity to MBYNE is shown by catalyst 4 of the lowest content of Cr, while the other three catalysts reveal similar selectivities. However, the selectivities decrease rapidly with time, except for catalyst 1, for which the drop is much slower. Selectivities to acetylene and acetone are significantly different for the particular catalysts at the beginning of the process. They increase with time and, surprisingly, tend to equalize for all samples.

Such differences in the catalytic behavior of the materials may be explained as follows. Active sites in CrAPO-5 are sorption centers which slow diffusion of reactants into the channels (17). Thus, the conversion is somewhat lower than that over $AlPO_4$-5. However, active sites of $AlPO_4$-5 (structure defects) lose their activity extremely quickly, likely as a result of coking. Activity of Cr centers is more stable and is maintained for a longer period. High and almost constant selectivity values of MBYNE over $AlPO_4$-5 prove that this is the only product of the reaction proceeding in this system. For the CrAPO-5 materials, selectivity to MBYNE drops with reaction time. However, this decrease has to be considered as an apparent effect because the high temperature of the process favors cracking reactions. The parallel decrease in selectivity to MBYNE and increase in selectivity to acetylene and acetone suggests that the main product, MBYNE, may undergo a consecutive cracking reaction resulting in these two light molecules. A higher yield of acetone suggests that a part of acetylene is consumed in a polymerization process which might be responsible for the observed coking. Such processes are not possible over $AlPO_4$-5 due to its too-weak acidity.

The observed differences between the examined CrAPO-5 samples also suggest an important role of Cr distribution, which causes variations in accessibility of the Cr centers to the reactants. The products formed on the centers located at external surface of the crystals can more easily leave the reaction zone and a consecutive cracking reaction is less probable than in the channels. Whatever the case is, as long as the active sites are not covered with coke deposits (primarily formed on acidic centers (23)), one can observe more MBYNE among the products. However, from the presented changes in the yield and selectivity of particular products, it is not possible to estimate what part of MBYNE was formed inside the CrAPO-5 channels or on the external surface and what part was cracked.

Samples 5 and 6 showed a similar behavior (Table 3) although the selectivity to MBYNE did not fall so rapidly. The results suggest either that these catalysts contain more acidic centers (23, 24) taking part in the formation of MBYNE or that there are other acidic centers which undergo coking to a lower extent. These are likely the multivalent extraframework Cr species (16–19). As they clog the channels, the reaction has to run primarily in the limited space of a surface layer of the crystals and, consequently, on a lower number of active sites. Thus, the sites should have a higher acidity. The increase in selectivity to acetylene and acetone over samples 5 and 6 is comparable to that over samples 1–4, which suggests that both products are formed over the HS and LS materials in a similar way. All these observations strongly support the conclusion that acetylene and acetone are most probably formed via decomposition of MBYNE in a consecutive cracking reaction over acidic sites.

From the point of view of incorporation of Cr, the changes of conversions and selectivities for the particular samples suggest that sample 4 of the lowest content of Cr reveals the most perfect incorporation of Cr and, consequently, the most perfect structure of the pores, and the highest possibility for diffusion. As opposed to that, sample 1 with the highest content of Cr contains probably a small fraction of extraframework Cr and, therefore, it gives effects more similar to those in samples 5 and 6 than in the other HS materials.

The yield of the isopropanol conversion (Tables 5 and 6) varies between 50 and 98% and propene is almost the only

TABLE 5

Conversion of Propanol-2 over CrAPO-5 Samples 1–4 (Table 1)

Time (h)	Conversion (%)				Selectivity (%)											
					Propene				DIPE				Acetone			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
0	92.13	64.61	50.20	94.00	99.24	98.28	95.83	98.00	0	1.20	1.96	1.51	0.76	0.53	0.66	0.49
1	91.81	60.50	55.22		98.40	97.97	97.56		0.94	1.49	1.92		0.66	0.54	0.52	
2	92.32	70.31	56.09		98.50	97.88	97.56		0.94	1.48	1.93		0.56	0.64	0.50	
3	92.27	72.01	57.31		98.48	97.84	97.56		0.98	1.52	1.93		0.54	0.64	0.51	
4	92.74	78.18	58.15		98.67	97.81	97.54		0.94	1.48	1.94		0.39	0.71	0.52	
5			58.84				97.60				1.93				0.47	
6			59.14	98.00			97.59	98.00			1.93	1.48			0.49	0.52

TABLE 6

Conversion of Propanol-2 over CrAPO-5 Samples 5 and 6 (Table 1)

Time (h)	Conversion (%)		Selectivity (%) Propene		DIPE		Acetone	
	5	6	5	6	5	6	5	6
0	73.88	56.57	97.01	96.26	2.06	2.74	0.93	1.00
1	78.70	86.35	97.74	97.32	1.73	2.01	0.53	0.67
2	79.72	87.07	97.82	97.36	1.71	1.99	0.47	0.65
3	80.68	87.42	97.76	97.47	1.70	1.97	0.54	0.56
4	81.10	87.95	97.43	97.38	1.71	1.98	0.51	0.64
5	81.77	88.30	97.81	97.38	1.67	1.98	0.51	0.64
6	82.06	88.52	97.94	97.49	1.66	1.98	0.40	0.53

product. Correlation between the yield of conversion and Cr content of the catalyst is similar to that in the case of MBOH, i.e., the conversion increases with the Cr content except for sample 4 with the lowest amount of Cr. The differences in relation to MBOH are that (i) the yield does not decrease with time but slightly increases in the initial period and then stabilizes at a constant level and (ii) the differences in the conversion due to the content of Cr are much higher. The selectivities to propene are stable or vary within a narrow range between 95 and 99%. Acetone and diisopropylether (DIPE) form in amounts below 1% (Table 6), indicating a marginal role of basic centers in this reaction. The conversion of isopropanol over $AlPO_4$-5 (Table 7) is similarly high at the beginning, but it drops considerably with reaction time, while selectivity to propene stabilizes at 100%.

All these results support the conclusions from the conversion of MBOH and prove that all the CrAPO-5 samples (Table 1) should have acidic centers. The most important is that the conversion of isopropanol confirms the absence of basic centers in CrAPO-5. Therefore, acetylene and acetone originate, in fact, from cracking of MBYNE. As acidity of all the catalysts is sufficient for this reaction, the differences in the conversion have to result from varying distribution of or accessibility to active sites. Thus, the highest, in average, conversion over the HS materials indicates the best accessibility to active sites, while the differences between particular samples reflect likely varying distribution of the sites. Lower conversions over the LS samples confirm a limited accessibility to active sites (clogged pores). The rapid decrease in the yield of the conversion over $AlPO_4$-5 is caused by coking.

TABLE 7

Conversion of Propanol-2 over $AlPO_4$-5 (Table 1)

Time (h)	Conversion (%)	Selectivity (%) Propene	DIPE	Acetone
0	97.79	98.30	1.12	0.52
1	94.33	98.52	0.99	0.49
2	89.01	100.00	0	0
3	85.00	100.00	0	0
4	77.00	100.00	0	0
8	49.00	100.00	0	0

CONCLUSIONS

The Cr(III) ions incorporated as heterocenters into an AFI-type structure reveal, in spite of the lack of an additional framework charge, increased acidity in comparison to the framework of $AlPO_4$-5 with structure defects. This is likely due to two additional water ligands at Cr, which are located in the pores and complement the coordination sphere of chromium to the favored (pseudo)octahedral one. The conversion of 2-methyl-3-butyn-2-ol (MBOH) requires a temperature above 573 K, at which there proceeds the consecutive reaction of cracking of the main product, 3-methyl-3-buten-1-yne (MBYNE), to acetylene and acetone on the acidic sites of CrAPO-5. The conversion of isopropanol can proceed at a lower temperature (553 K) and does not give such an effect, yielding almost exclusively propene as the product. The yield of the conversion follows, in general, the content of chromium in CrAPO-5, but it is dependent also on the distribution of the Cr centers.

The materials with extraframework chromium (multivalent Cr species clogging the pores) also reveal an acidity higher than that of nonsubstituted $AlPO_4$-5. The conversion over these Cr species results in products and effects similar to that over the framework Cr, but it is lowered by (i) hindered accessibility inside the clogged pores and (ii) a faster coking. No basic centers are created in the investigated Cr-containing materials, as concluded from the isopropanol conversion.

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