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CONVERSION OF C_8 AROMATICS AND n-PENTANE OVER Ga_2O_3/HZSM-5 MECHANICALLY MIXED CATALYSTS

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Ga_2O_3/HZSM-5 catalysts prepared as intimate physical mixtures of Ga_2O_3 with HZSM-5 have been studied for the conversion of C_8 aromatics and the aromatization of n-pentane. Hydrogen reduction of the mechanical mixture is a necessary step in the formation of an active catalyst and the reduction process has been characterized by IR spectroscopy. Reduced materials exhibit superior activity and selectivity compared to mechanical mixtures which have not be reduced.

Keywords: Gallium-ZSM-5 system catalysis, HZSM-5 catalyst, KPD-2 catalyst, pentane conversion, C_8 aromatic isomerization, infrared spectra of HZSM-5 catalyst, infrared spectra of KPD-2 catalyst

1. Introduction

Recent interest in light paraffin aromatization over Ga containing ZSM-5 catalysts is largely a result of the announcement of the Cyclar process [1]. Several different methods have been reported to be effective for the manufacture of Ga containing catalysts including ion-exchange [2], impregnation [3], and ZSM-5 containing framework Ga [4]. Most reaction studies have focused on C_2–C_4 paraffin aromatization though n-pentane aromatization [5] has received some attention.

We have prepared intimate mechanical mixtures of Ga_2O_3 and HZSM-5 and tested these materials for propane aromatization [6,7]. H_2 reduction has been shown to be an important step in the activation of these mechanical mixtures for

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propane conversion [6] and previous microbalance reduction data [7] suggest that the reduction process proceeds via:

$$Ga_2O_3 + 2H^+Z^- + 2H_2 \rightarrow 2Ga^+Z^- + 3H_2O, \qquad (1)$$

where Z^- is an anion zeolitic site. If the Ga_2O_3 phase is consumed during the reduction process as in eq. (1), IR spectroscopy should be able to detect this change. Therefore, we report here the characterization of the zeolite via IR spectroscopy and provide further evidence of a link between catalytic activity and Ga reduction through C_8 aromatic isomerization and n-pentane aromatization reactions.

2. Experimental

Catalysts were prepared by ballmilling β-Ga_2O_3 (4N5 grade, Ingal International Co.) with HZSM-5 (Linde ELZ-106-6). The manufacturer reported composition of the zeolite was 94.95% SiO_2, 3.73% Al_2O_3 and 0.03% Na_2O by weight. A catalyst containing 2% Ga on an elemental basis was prepared. We refer to this material as KPD-2 where the numerical suffix indicates the gallium loading in wt%. Catalysts were pelletized crushed and sieved to 40–60 mesh prior to use.

Catalyst evaluation was performed in fixed bed continuous flow microreactor at atmospheric pressure. About 0.5 g of catalyst was loaded in the reactor and treated with air (4 hours) followed by N_2 at 773 K. In some cases, an additional reduction at 773 K for 1.5 hours with H_2 gas was performed; these catalysts are referred to as "reduced". Nitrogen was used as a diluent gas for hydrocarbon conversion reactions and the N_2/HC ratio for C_8 conversion reactions was 3 while the n-pentane partial pressure during n-C_5 conversion was 3.9 kPa. An industrial feed was used in the C_8 aromatic isomerization reaction. The analysis of the feed and the reactor products was performed in all cases with a Hewlett-Packard 5890 GC equipped with a FID detector, 50 m PONA capillary column and automated gas sampling valve injection. An M80 Carl-Zeiss spectrometer was used for IR spectroscopy. The gallium oxide content in the fresh and "reduced" catalysts was determined by IR using KBr-pellets and applying a new analysis technique which is described in detail in ref. [8].

3. Results and discussion

n-PENTANE CONVERSION

The conversion of n-pentane under the prevailing experimental conditions (low n-pentane partial pressure) leads to two primary groups of products: C_1-C_4 paraffins and olefins and C_6-C_8 aromatic hydrocarbons along with small amounts

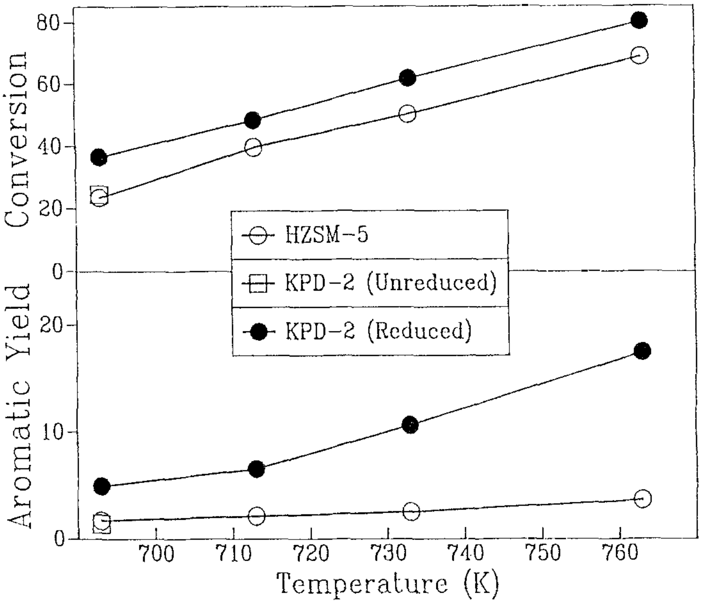

Fig. 1. n-pentane conversion over HZSM-5 and KPD-2 catalysts.

of C_5 olefins, i-pentane and C_9 aromatics. Results are shown in fig. 1. Over HZSM-5 in the temperature range 693-763 K, cracking products predominate and there are only small amounts of aromatic hydrocarbons. The introduction of 2 wt% Ga via mechanically mixing gallium oxide with HZSM-5 alone does not significantly alter the initial (short time-on-stream) catalytic activity and selectivity at 693 K. Observations at short time-on-stream limits the possible reduction of the gallium oxide component by the products of n-pentane conversion [7].

After the initial catalytic testing, the same KPD-2 sample was purged with N_2 for 0.5 h at 773 K and reduced in the catalytic reactor for 1.5 h with pure hydrogen at this temperature. As shown in fig. 1, a strong enhancement in aromatization activity (by a factor of about 5) at 763 K is the most important effect of Ga addition and reductive treatment. In the case of n-pentane conversion at 693 K, the catalytic results confirm the role of the H_2 reduction in creating a new active state of the Ga containing ZSM-5 zeolite catalysts. The effect of the hydrogen reduction was previously observed in the case of the propane conversion on mechanically mixed Ga_2O_3 catalysts [6,7].

The detailed analysis of the hydrocarbon products shown in table 1 gives additional information regarding some intrinsic features of the catalytic system formed by the reductive treatment. For example, from table 1 it is to be seen that hydrogen reduction strongly influences both isobutane/n-butane and olefin/paraffin ratios of the hydrocarbon product while the distribution of the aromatic hydrocarbons and methane production change very little. Gnep and coworkers have compared the product composition in the case of propane conversion on

Table 1

Pentane conversion. WHSV = 1.8 h^{-1}

				KPD-2	KPD-2
Catalyst	HZSM-5	HZSM-5	KPD-2	Reduced	Reduced
Temperature, K	693	713	693	693	713
Pentane conversion, %	23.4	39.5	24.5	36.5	48.1
Aliphatics, wt.%	21.7	37.4	23.1	31.6	41.6
Aromatics, wt.%	1.7	2.1	1.4	4.9	6.5
Distribution of C_1-C_4%					
C_1	1.9	2.5	1.9	2.7	3.6
C_2	27.8	32.3	27.6	26.7	28.9
C_3	49.3	48.3	48.9	45.6	43.9
C_4	21.0	16.9	21.6	25.0	23.6
Key ratios:					
Ethylene/Ethane	1.59	1.51	1.60	1.11	1.46
Propylene/Propane	0.55	0.64	0.53	0.40	–
Butenes/Butanes	0.91	1.16	0.93	0.35	0.39
Isobutane/n-Butane	0.53	0.60	0.55	1.57	2.00
Distribution of BTX aromatics					
Benzene	15.7	16.0	12.7	17.5	17.2
Toluene	43.3	44.0	43.0	41.6	39.2
Xylenes + Ethylbenzene	41.0	40.0	44.3	40.9	43.6

HZSM-5 and GaHZSM-5 prepared by impregnation of HZSM-5 with gallium nitrate [3]. They observed similar effects consisting of increased paraffin/olefin and isobutane/n-butane ratios from the reaction product over GaHZSM-5 and explained this effect in terms of dehydrogenation activity of the gallium oxide, which increases both propane activation and naphthene aromatization [3]. However, no explanation was given by Gnep et al. regarding the enhancement of the isobutane/n-butane ratio. Since we are not able to detect any significant changes in the product composition in the case of n-pentane conversion on the nonreduced KPD-2 catalyst versus the pure HZSM-5, we cannot confirm the contribution of Ga_2O_3 alone in this process. Furthermore, we suggest that the activation of the catalyst either by hydrogen prior to the reaction or by the hydrogen product of the conversion of a paraffin appears to be the most important factor for the development of aromatization activity. The importance of this activation process is also reflected in the relative yields of other hydrocarbon products which change drastically as a result of the reductive pretreatment. After hydrogen reduction, the catalyst is more able to produce saturated hydrocarbons and isobutane along with aromatic hydrocarbons. Generally, this feature of the reduced catalysts can be considered in terms of an increased ability of the catalysts to facilitate hydrogen transfer reactions [9].

CONVERSION OF C_8 AROMATICS

The results of the catalytic testing of HZSM-5, KPD-2 and reduced KPD-2 samples are presented in table 2 along with the composition of the C_8 aromatic feed. At the experimental conditions selected, a distribution of the xylene isomers close to the equilibrium value was obtained with all catalysts under investigation. The side reactions of disproportionation and dealkylation of the C_8 aromatics determine the final product composition. Except for slightly more benzene and toluene, data in table 2 indicate that there is virtually no difference between the products observed on the HZSM-5 sample and products resulting from the catalytic evaluation of the KPD-2 sample which has not been subjected to hydrogen reduction. Also, hydrogen treatment of the pure HZSM-5 sample prior to catalytic testing had virtually no effect on the catalytic properties of this sample. In contrast, hydrogen reduction of the KPD-2 sample leads to an enhanced rate of ethylbenzene conversion and to an enhancement in side reactions of xylene isomers as indicated by the increased xylene loss compared to the other two catalysts. KPD-2 maintains high activity for ethylbenzene conversion even after regeneration in air (sample KPD-2* reduced). This is a rather unexpected result because the conversion of C_8 aromatics is generally considered to be an acid catalyzed reaction and others have failed to confirm any significant effect of gallium introduction on the acidity of ZSM-5 zeolite [3]. The proposed bifunctional pathway of this reaction [3,10,11] which has generally been applied to light paraffin aromatization, but might also be considered important in C_8

Table 2

C_8 aromatic isomerization. WHSV = 1.5 hr^{-1}, 553 K

Catalyst		HZSM-5	KPD-2	KPD-2 Reduced	KPD-2 * Reduced
Product (feed) composition wt.%:	FEED				
Light Gases	–	0.02	–	0.01	–
Benzene		1.29	1.66	2.51	2.43
Toluene	1.41	1.77	1.95	2.54	2.29
Ethylbenzene	19.66	15.87	16.06	13.88	14.22
Xylenes	78.80	78.20	77.70	77.00	77.10
Ethyltoluenes	0.05	0.53	0.41	0.74	0.79
Trimethylbenzenes	0.02	0.47	0.33	0.45	0.49
Diethylbenzenes	–	1.21	1.19	1.65	1.62
Dimethylethylbenzenes	–	0.80	0.67	1.22	1.08
Other Aromatics	–	–	–	0.03	–
Ethylbenzene Conversion%		19.30	18.30	29.4	27.7

* After a regeneration of the KPD-2 sample at 773 K in air flow (no additional H_2 reduction after the regeneration was applied).

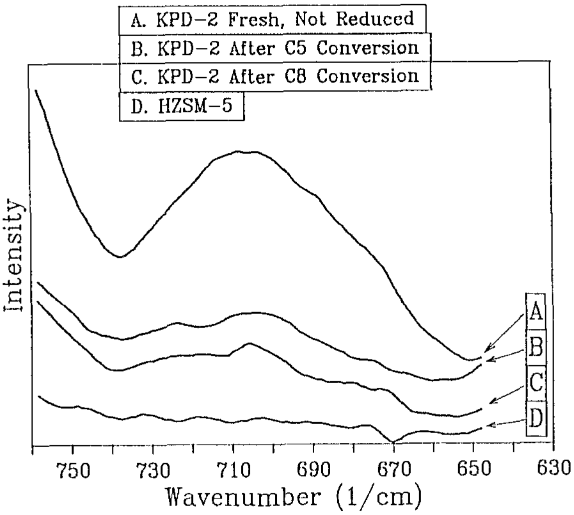

Fig. 2. Infrared spectra of HZSM-5 and KPD-2 catalysts.

isomerization, appears to be less probable because of the low loadings of gallium oxide used in this study. In addition, it is well known that gallium oxide possesses only a weak dehydrogenation function [11,12]. In our opinion, there is no doubt that the pretreatment with hydrogen plays a key role in creating a new active state of the catalyst. Since the disproportionation and transalkylation reactions require a bimolecular transition state, it is reasonable to assume that the new active state of the catalyst contributes to an acceleration of hydrogen transfer processes. The strong increase in the ethylbenzene conversion coupled with the relatively small xylene loss over the hydrogen treated Ga catalyst may be promising from a practical point of view.

IR EVIDENCE FOR THE REDUCTION OF Ga_2O_3

In a previous paper we have shown that X-ray diffraction is as a suitable tool for the semi-quantitative determination of the gallium oxide content in HZSM-5 zeolites [7]. Recently we have found, however, that an IR technique is more convenient for this purpose in cases where only a small quantity of sample exists or in the investigation of catalysts which have been used in catalytic reactions. in fig. 2, the IR-spectrum of the unreduced KPD-2 sample in the 700 cm^{-1} region is presented which clearly shows a broad band due to the gallium oxide crystalline phase. After treatment with H_2 followed by a hydrocarbon reaction, the band disappears completely which points to a dramatic change in the state of gallium. Treatment with H_2 alone (no hydrocarbon feed) shows an identical effect. Elemental chemical analysis of the catalysts indicates no significant decrease in the gallium content of the reduced catalyst. Thus, the IR spectra provide evidence that the treatment with hydrogen has altered the state of the catalyst to a new state which appears to be more suitable for catalyst reactions such as n-pentane aromatization and C_8 aromatic conversion.

4. Conclusions

Different techniques reported in the literature [2,3,4,10] as being suitable for the introduction of Ga into ZSM-5 to yield catalysts with enhanced aromatization activity has been interpreted as evidence of a bifunctional nature of these catalysts [3,10,11]. The gallium oxide species which is formed via thermal treatment of the catalysts in air or in an inert gas has been the locus of the catalyst function which ensures increased dehydrogenation activity [3,12], while acidic sites of HZSM-5 have been thought to be responsible for a number of reaction steps including cracking, oligomerization and cyclization [13]. However these theories assume that gallium oxide and acidic sites remain separate entities under catalytic conditions. We have recently reported evidence including XRD, microbalance reduction experiments [7], as well by XPS and IR techniques [14,15] that the gallium oxide phase interacts strongly with the acidic zeolite and shown that, in the case of mechanically mixed catalysts, this interaction as leads to a transfer of Ga into the zeolite. Moreover, the number of the acidic hydroxide groups of the HZSM-5 zeolite diminishes as a result of this interaction [15] and we expect that part of the zeolitic protons are replaced by new Lewis acid sites centered around gallium which is in an oxidation state lower than $+3$. In our opinion, the bifunctional theory needs to be revised to some extent in order to include the impact of the gallium oxide phase on the zeolite acidity. The enhanced catalytic activity for n-pentane and C_8 aromatic conversion after treatment of the mechanically mixed catalyst with hydrogen corresponds to the new active state of the catalyst which can not be explained in terms of the bifunctional action of the separate components of the mixed catalyst. Finally, further work is needed to elucidate in detail the mechanism of the catalytic action as well the increased capability of these catalysts to accelerate hydrogen transfer reactions as shown in the present investigation.

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