

Reactions of Hexene on Silica-Aluminas and Aluminas with Special Regard to Cyclization Reactions

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Cyclization, skeletal isomerization, and cracking of hexene-1 were investigated using several pure, chlorinated, and fluorinated γ -aluminas, η -alumina, and different silica-aluminas. From deactivation measurements and the dependence of activities on known Lewis and Brønsted acidities of different catalysts the following conclusions were proposed: Skeletal isomerization, cracking, and formation of higher molecular compounds are best catalyzed by Brønsted centers. Formation of methylcyclopentane takes place on these centers too, but its rate of formation is higher on pure alumina where it is probably caused by Lewis centers. All the other reactions are also catalyzed by pure alumina. There are at least two types of centers on alumina that has been pretreated at 530°C. On silica-alumina, cyclization—leading to five-membered rings only—is believed to take place with the methylcyclopentyl cation as an intermediate. This ion is stable for a longer time on Brønsted sites enabling the addition of another hexene molecule to occur. Further reaction of these products lead to higher molecular weight which in turn leads to an asymmetry in the distribution of cracking products and to coking. On pure alumina a methylcyclopentyl complex seems to be less stable, it desorbs as methylcyclopentane. Moreover it was observed that the coking of the catalyst increased in the same way as the formation of dimethylcyclopentane or the deficit of methane or ethane. A possible explanation for this fact is that higher molecular products like methyl-ethylcyclopentanes, which should be expected according to the ethane deficit but were not found, may react to form coke. The fact, that different methylcyclopentenes play an important role in coking was further confirmed by experiments with methylcyclopentene as a feed. Deactivation and forming of coke was much faster under these conditions than with hexene-1.

1. INTRODUCTION

Alumina is a widely used active carrier used in reforming catalysis. As could be shown by several authors (1-3), isomerization, dehydrocyclization, and cracking on a reforming catalyst (Pt on Al_2O_3) occur to a remarkable extent via bifunctional mechanisms, including both the hydrogenating-dehydrogenating and the acidic functions of the catalyst. Furthermore direct evidence was obtained that activated aluminas catalyze reactions involved in the reforming process, like skeletal isomerization (4-9); cyclization of alkenes (2, 3); and cracking of alkanes (10), cycloalkanes (11, 12), and alkenes (13). From a commercial viewpoint the production of high-octane-number

fuels, isomerization and cyclization reactions are of special interest. While skeletal isomerization of alkenes is generally believed to take place on Brønsted sites (4, 5), there is some doubt whether the same is true for the cyclization reactions (3). Until now all attempts have failed to detect Brønsted acid sites on alumina directly, possibly because of their low concentration. For example, Pary (14) and Knözinger and Kaerlein (15) could not find pyridinium ions in their infrared spectroscopical studies of pyridine adsorption on alumina. On the other hand, the existence of Brønsted acid sites on silica-aluminas is well established by ion exchange with sodium chloride (16) or with ammonium acetate (17), as well as by infrared spectroscopical investigations showing the ex-

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istence of ammonium or pyridinium ions on the surface (14, 18, 19). The reactivity of silica-aluminas clearly correlates with their Brønsted site concentration for polymerization of propylene (20), cracking of cumene (21), and isomerization of *o*-xylene (20, 22). According to Pines and Haag (4, 5) the skeletal isomerization of alkenes takes place via a classical carbonium ion mechanism with successive steps of 1,2-methyl shifts. This is not in accord with the observation that 3-methylpentene is a primary product from hexene isomerization (23). Moreover the existence of different centers for skeletal isomerization and cyclization on alumina has been reported (23).

η -Alumina was found to be more active in isomerization reactions of alkenes than γ -alumina (7). The activity of aluminas for the typical reforming reactions may be increased by partial chlorination of the catalyst surface (24). From comparison of reaction products and product ratios for different catalysts, namely, γ - and η -aluminas, chlorinated and fluorinated aluminas and silica-aluminas, we hoped to obtain more information about the different sites and the reaction mechanisms.

2. EXPERIMENTAL

2.1. Catalysts

Besides using commercial γ -alumina (Merck), γ - and η -aluminas were prepared by calcination of boehmite ($\text{AlO}(\text{OH})$) and bayerite ($\text{Al}(\text{OH})_3$) (25–27). Silica-aluminas were prepared by

(a) coprecipitation from sodium silicate and aluminum-chloride solutions and

(b) mixing the gels obtained from aluminum nitrate and ammonia and from the tetraethylester of silicic oxid and nitric acid. Pure silicas and aluminas, obtained in the same way, were also investigated.

The surfaces of the oxides were purified from chlorine using ammonia and from alkali by a nitric acid treatment and subsequent washing with double distilled water.

Chlorine- and fluorine-containing alu-

minas were prepared from the commercial alumina sample by treatment with aqueous solutions of hydrochloric or hydrofluoric acid; the dried samples were subsequently heated to 530°C in air.

2.2. Experimental Procedure

A carrier gas stream (He or H_2 , 50 Nml/min) was passed over heated Cu on silica (BTS-catalyst) to remove traces of oxygen and was dried over P_2O_5 on silica (Sicapent) and then passed through a cold trap filled with molecular sieve (3 Å at -196°C). One part of the carrier gas was loaded with hydrocarbon.

The reactants were passed over the catalyst, which had been pretreated at 530°C for 1 h, at reaction temperatures of 350 to 400°C at normal pressure. Usually the reaction products were hydrogenated in a small second reactor. The hydrocarbons obtained were analyzed gas chromatographically using a 25-m squalan capillary column at room temperature. The hydrocarbons used had a purity >99% and were dried over a molecular sieve (3 Å) before use.

3. RESULTS AND DISCUSSION

Deactivation measurements were made for different types of reactions on various catalysts. The behavior of an alumina catalyst containing 0.38% Cl is shown in Fig. 1. The deactivation of the isomerization reactions is much slower than that of either the cracking or the formation of methylcyclopentane (MCP) reactions. This behavior, observed with chlorine-free γ -alumina as well as with silica-aluminas, shows that at least two types of centers are active on these oxidic catalysts. These results were confirmed by measurements with silica-alumina catalysts produced in a different way (Table 1).

The rates for the isomerization reactions are different for the two types of oxides, while those of the cyclization reaction are equal within the limits of error.

The following hydrocarbons were identified following the hydrogenation of

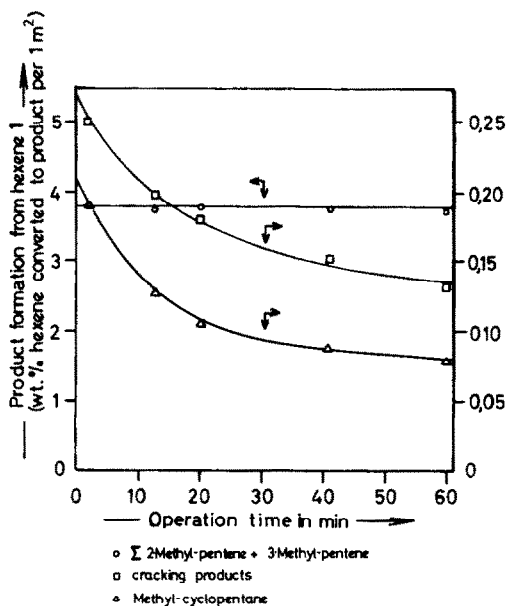


FIG. 1. Deactivation behavior of γ - Al_2O_3 -0.38% Cl during the reaction of hexene-1 at 370°C .

the primary reaction products of hexene-1: methane, ethane, propane, butane, pentane, 2- and 3-methylpentane, and methylcyclopentane. Isobutane, isopentane, 2,2- and 2,3-dimethylbutane were formed as secondary products. Cyclohexane was not observed.

Besides the substances mentioned above, smaller amounts ($\leq 2\%$) of products containing more than six carbon atoms were formed. About 20% of these products were dimethylcyclopentanes. The amount of these products varied with the type of catalyst.

TABLE 1

Reactivity^a of Silica-Aluminas Prepared in a Different Way

Oxide	Isomerization 2-MPe + 3-MPe	Cyclization MCP + DMCP
Coprecipitated		
SiO_2 - Al_2O_3 (60:40)	52.6	0.012
SiO_2 - Al_2O_3 (88:12)	26.0	0.010
Mixed gels		
SiO_2 - Al_2O_3 (60:40)	13.1	0.012
SiO_2 - Al_2O_3 (90:10)	9.0	0.012

^a Moles of product formed from 100 moles of hexene-1 on 1 m^2 of catalyst at 370°C ; contact time: 0.01 sec.

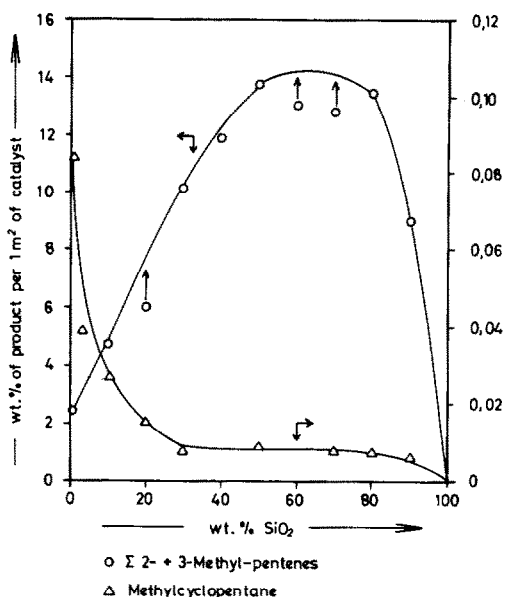


FIG. 2. Formation of isomerization and cyclization products from hexene-1 on silica-aluminas.

Figures 2 and 3 show the activity of silica-alumina catalysts with different contents of SiO_2 for the isomerization and cracking reactions. Comparing these results with the Lewis and Brønsted acidities of silica-aluminas (29) one finds that activities

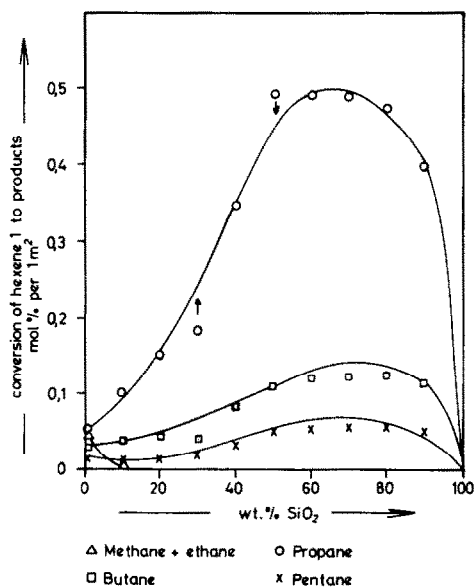


FIG. 3. Formation of cracking products from hexene-1 on silica-aluminas.

for isomerization to 2- and 3-methylpentanes and cracking reactions leading to propane, butane, and pentane correlate with Brønsted acidity while formation of methane, ethane, and the main part of methylcyclopentane formation decreases with SiO₂ content as does the Lewis acidity. From the fact that no Brønsted acid sites could be found on pure alumina (14, 15) one might conclude that in this case the reaction mentioned are catalyzed by Lewis acid centers. But one must be careful because other types of centers (defect centers, basic centers, or acid-base pairs) may play a role, although, at a pretreatment temperature of 530°C, the number of such centers should be small (30). From Fig. 1, on the other hand, it follows that there are different types of sites on the alumina.

Aluminas containing chlorine are known to have more active Lewis sites as compared to pure alumina but no Brønsted sites (15). This is in contrast to fluorided aluminas which show Brønsted acidity (28).

As is to be expected, the reactivity of alumina was increased unselectively by chlorination. Fluorination, in contrast, increased the isomerization rates drastically, leaving the other reactions almost un-influenced (Table 2).

In Fig. 4 one may see the formation of cyclic compounds over different silica-alumina catalysts. Methylcyclopentane is formed on both catalysts with high Lewis as

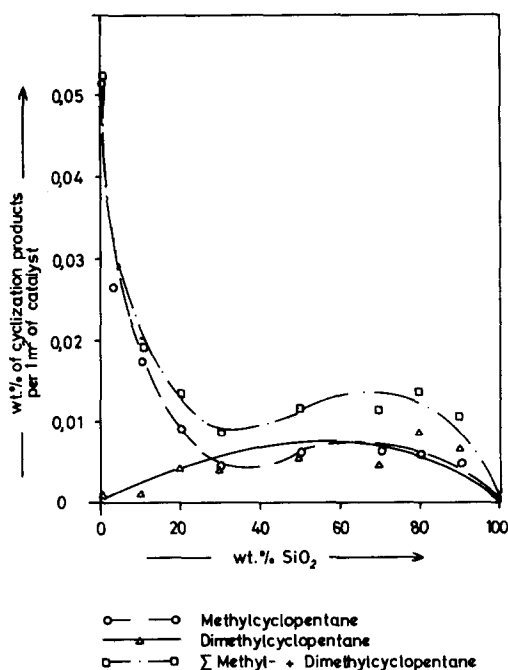


FIG. 4. Formation of cyclic compounds on silica-aluminas.

well as on catalysts with high Brønsted site concentrations; the dimethylcyclopentanes are predominately formed on the Brønsted sites.

It is interesting that, in contrast to what one might expect, the amount of methane formed is less than that of the pentanes. The same is true for ethane and the butanes. From Fig. 5 one can see that the lack of methane and ethane correlates with silica

TABLE 2

Reactivities^a of Different Catalysts at 370°C

Oxide	Isomerization		Cracking			Cyclization	
	2-MPe	3-MPe	Pr	Bu	Pe	MCP	DMCP
γ -Al ₂ O ₃ (Merck)	0.85	0.85	0.02	0.01	0.001	0.081	—
γ -Al ₂ O ₃ (Boehmite)	1.16	1.02	0.05	0.03	0.01	0.110	—
η -Al ₂ O ₃	2.21	2.14	0.02	0.01	0.002	0.024	—
γ -Al ₂ O ₃ 0.5% Cl	1.40	1.35	0.02	0.02	0.003	0.110	—
γ -Al ₂ O ₃ 1.0% F	21.70	19.46	0.83	0.06	0.04	0.140	Traces
SiO ₂ : Al ₂ O ₃ (60:40)	6.99	6.04	0.52	0.12	0.07	0.06	0.006

^a Moles of product from 100 moles of hexene-1 over 1 m² of catalyst.

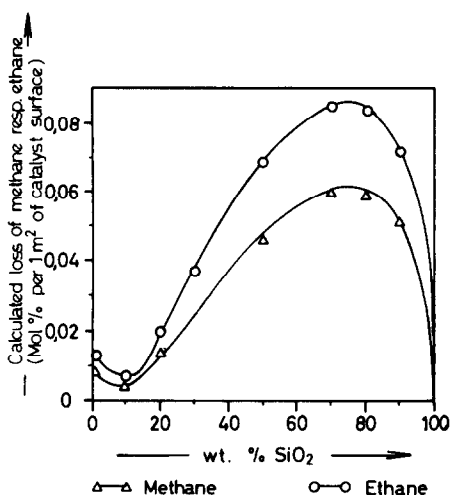


FIG. 5. "Deficiency" of methane and ethane in the reaction products formed from hexene-1 at silica-aluminas.

content; the deficiency of methane is about as great as the amount of dimethylcyclopentanes formed. These observations may be explained in the following way: methylcyclopentyl cations or complexes are formed on alumina as well as on silica-aluminas. The complex on alumina is less stable and is desorbed in form of methylcyclopentane. On silica-aluminas, where the mean lifetime of the ion is longer, a further reaction is possible and two hexenes may react to form a dimer methyl-hexyl-cyclopentane ion. This is cracked and after hydrogenation gives either pentane and dimethylcyclopentane or butane and methylethylcyclopentane. These are not observed directly but undergo further reactions leading to coking products. Unpublished measurements (31) show that methylcyclopentanes as well as methylcyclopentenes are formed together with the complementary pentenes and pentanes.

The conversions to dimethylcyclopentanes were low, but from the reproducibility of the measurements and from the different values obtained for different catalysts, it could be shown that the results were no artifacts.

The deactivating cation of cyclic com-

pounds could be confirmed using methylcyclopentene as a feed; under these conditions the deactivation of the catalyst was much faster than with hexene. The product ratio 2-methylpentene/3-methylpentene (2-MPe/3-MPe) also indicates a change of mechanism in going from silica-aluminas (2-MPe/3-MPe = 1.14–1.17) to pure alumina (2-MPe/3-MPe = 0.97). The first ratio characteristic of reactions on Brønsted centers was also observed for reactions on fluorinated alumina. On chlorinated alumina this ratio is 1.03. This is a further proof that on pure, as well as on chlorinated aluminas, the concentration of active Brønsted centers must be very small if in fact there are any centers of this kind at all.

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