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Adsorption Measurements during Competitive Isomerization of Olefins over KC_{24}

INTRODUCTION

Much attention has been paid to the catalytic properties of graphite intercalation compounds, which have extensively been investigated in various reactions (*1*, *2*). Adsorption plays an important role in heterogeneous catalysis, and the measuring adsorption during the reaction have been fruitful in many investigations (*3*, *4*). In this study the interest has centered on the catalytic characteristics of KC_{24} for the isomerization of olefins with emphasis on elucidating the reaction selectivity.

EXPERIMENTAL

Materials. The KC_{24} samples as a catalyst were prepared in the similar manner as described elsewhere (*5*). The graphite (1.25 g of Union Carbids Spectroscopic Grade powder) and 0.44 g of potassium metal were used for each preparation. The preparation vessel was heated in a electric heater for 24 h at 620 K to form KC_{24}, and then evacuated for 30 min. The X-ray diffraction data of the samples formed agreed quite well with those reported by Rüdorff and Schultze (*6*). The KC_{24} obtained was deep blue.

Olefins used as the reactants were obtained from Tokyo Kasei Company, Ltd., and were purified by repeated distillation *in vacuo,* and the purity was confirmed by gas chromatography to be more than 99%. Helium (99.995%) and nitrogen (99.99%) were obtained from the Seitetsu Kagaku Company, Ltd.

Procedure. The apparatus and procedure used for the present study were essentially the same as that used previously (*4*). A closed circulating system with greaseless stopcocks and with a U-shaped reactor, connected to a conventional vacuum line and a gas chromatograph, was used to follow the course of the reaction. The volume of reaction system corresponded to about 288 cm^3 at a reaction temperature 373 K. The reaction mixtures were occasionally analyzed by gas chromatography.

The amounts of adsorption were obtained from the material balance, as was previously described (*4*). When the 1-butene, for example, was the reactant, amounts of adsorption were estimated from the amount of 1-butene introduced and the pressure and the composition of the circulating gas at the suitable time. The sum of butenes adsorbed could only be estimated. When the mixture of olefins was used as the reactant, the material balances were calculated for each reactant olefin.

RESULTS AND DISCUSSION

The competitive isomerization of olefins over the KC_{24} has been studied, two kinds of olefins being combined. The isomerization reaction did not take place over either of the potassium–graphite, but took place over the intercalation compound under the same experimental conditions. The results suggest that the catalytic activity is due to the charge-transfer effect, because the alkali metal–graphites can be considered as charge-transfer complexes (*2*).

Figure 1 shows a typical result of the competitive isomerization of 1-butene and 1-hexene over KC_{24} at 440 K. The induction period is observed for both 1-pentene and 1-hexene.

The amount of adsorption of 1-pentene in

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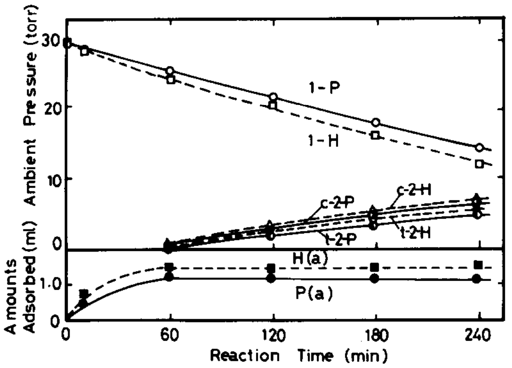

FIG. 1. Competitive isomerization of 1-pentene and 1-hexene at 440 K over KC_{24}. Olefins in the gas phase; 1-pentene (○), 1-hexene (□), *cis*-2-pentene (◑), *trans*-2-pentene (◐), *cis*-2-hexene (△), and *trans*-2-hexene (▽). Olefins adsorbed; pentenes (●) and hexenes (■).

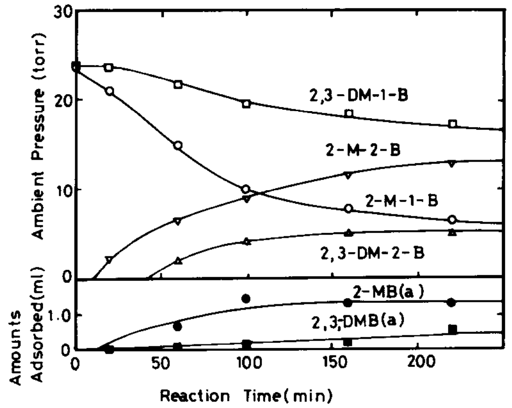

FIG. 2. Competitive isomerization of 2-methyl-1-butene and 2,3-dimethyl-1-butene at 453 K over KC_{24}. Olefins in the gas phase; 2-methyl-1-butene (○), 2,3-dimethyl-1-butene (□), 2-methyl-2-butene (▽), and 2,3-dimethyl-2-butene (△). Olefins adsorbed; 2-methylbutenes (●) and 2,3-dimethylbutenes (■).

the presence of 1-hexene was less than that in the absence of 1-hexene. The result suggests that the adsorption of 1-pentene is disturbed by the presence of 1-hexene, and that 1-hexene is more strongly adsorbed on the same kind of sites than 1-pentene in the competitive adsorption during the reaction.

The rate of isomerization of 1-pentene just after the induction period is less than that of 1-hexene. The initial rate and the amount of adsorption of 1-pentene were also less than those of 1-hexene. The results suggest that the higher reactivity of 1-hexene than 1-pentene is due to either the greater rate of adsorption, or the greater amount of adsorption of 1-hexene, or both.

Figure 2 shows a typical time course of the competitive isomerization of 2-methyl-1-butene and 2,3-dimethyl-1-butene over KC_{24} at 453 K. 2-Methyl-1-butene was much more reactive than 2,3-dimethyl-1-butene, which is consistent with the initial rate and the amounts of adsorption during the reaction.

The isomerization of olefins after the induction period was almost first order with respect to the pressure of reactant ranging from 15 to 100 Torr. The relative rate constants of olefins at 400 K and the activation energies were determined as shown in Table 1. No gaseous hydrocarbon other than olefin could be detected.

The reactivity of 1-olefins seemingly increased with increasing the number of carbon. The tendency agrees with the adsorption behavior during the reaction; the more

TABLE 1

Relative Rate Constants at 400 K and Activation Energies over KC_{24}

Reactant	Product	k	E_a (kJ/mol)
1-H	c + t	244	16
	c-2-H	174	12
	t-2-H	70	21
1-P	c + t	140	31
	c-2-P	93	30
	t-2-P	47	33
2-M-1-P	2-M-2-P	57	38
1-B	c + t	100[a]	33
	c-2-B	73	25
	t-2-B	27	46
2-M-1-B	2-M-2-B	77	33
3-M-1-B	2-M-1-B, 2-M-2-B	36	42
	2-M-1-B	4	50
	2-M-2-B	32	33
2,3-DM-1-B	2,3-DM-2-B	22	50

[a] Corresponded to 2.60×10^{-3}/g.

adsorbed olefin was more reacted. Based on the selectivity ratio, *cis/trans*, the isomerization of 1-olefins over KC_{24} may proceed with a π-allylic carbanion mechanism, which is typically operative over basic catalysts (*7*, *8*). The variation in k is less than 2.5 between the fastest (1-hexene) and the slowest (1-butene). The small difference may be due to the same reaction mechanism.

The branched olefins are less reactive than normal olefins. The order of reactivity does not depend on the number of carbon, but the degree of methyl substitution. The minimum dimension of *n*-olefin molecules is 2.8 Å, and that of monomethyl–olefin molecules is 3.6 Å, while that of dimethyl-olefin molecules is 5.2 Å. The olefin molecules became fat by the methyl substitution. Since the interlayer distance of KC_{24} is 5.4 Å, the fat molecules are probably more difficult to penetrate into the space of graphite lattice layers and less reactive than lean molecules. The minimum dimension of 2-methyl-1-butene and 3-methyl-1-butene is the same, but the reactivity was a little bit different. The fact suggests that other kind of effect than molecular dimension may contribute to the reaction. The amount of adsorption of the more reactive olefin was greater than that of the less reactive one. These results are reasonable, since all the effects influencing on the reactivity are integrated into the adsorption during the reaction.

CONCLUSION

The competitive isomerization revealed that the reactivity of 1-olefins increased with increasing the number of carbon, and that by methyl substitution the reactivity of olefins decreased. The amount of adsorption of the more reactive olefins is greater than that of the less reactive one.

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