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INFLUENCE OF METHANOL ADDITION DURING SELECTIVE HYDROGENATION OF BENZENE TO CYCLOHEXENE

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Abstract

The addition of a certain methanol concentration during benzene hydrogenation on Ru/Al_2O_3 improves the selectivity to cyclohexene because of a preferential adsorption of methanol on the most active Ru sites.

Keywords: Methanol, selective hydrogenation

INTRODUCTION

The partial hydrogenation of benzene to cyclohexene has been of much interest in recent years [1-3]. Cyclohexene, which has a highly reactive double bond, is used as an intermediate material for producing nylons and fine chemicals. Cyclohexene can be obtained by several methods such as dehydration of cyclohexanol. These processes require complicated multiple steps, thus leading to high production costs. Meanwhile the selective hydrogenation of benzene requires only one step and is more adequate from an industrial point of view. During the selective hydrogenation of benzene to cyclohexene in the liquid phase the selectivity to cyclohexene can be increased by the addition of reaction modifiers [4]. Such modifiers stimulate desorption of cyclohexene and/or slow down its further hydrogenation to cyclohexane.

The objective of this paper is to analyze the influence of the addition of methanol in different concentrations on the activity and selectivity of a Ru/Al_2O_3 catalyst prepared using $RuCl_3$ as precursor.

EXPERIMENTAL

Catalyst preparation

The catalyst was prepared by incipient wetness impregnation [5] of Al_2O_3 Ketjen CK 300 (Sg = 200 m^2 g^{-1}, cylinders of 1.5 mm diameter and 4.0 mm length) using a $RuCl_3$ (Strem Chemicals) solution of a concentration such as to obtain a catalyst containing 4 wt.% ruthenium. The sample was dried, calcined at 773 K for 3 h, washed and reduced at 673 K for 6 h.

Catalyst characterization

Ruthenium content on the catalyst was determined spectrophotometrically using a methanol solution saturated with *N*,*N*'-diphenylthiourea (DPTU), based on the Ru capacity to form a complex with DPTU under certain conditions [6].

Ruthenium dispersion was measured in a volumetric equipment at 373 K. Each point was measured after 5 min stabilization. For calculations, a H:Ru atomic ratio equal to 1 was used.

Catalytic test

The selective benzene hydrogenation reaction was carried out in a stainless steel stirred tank reactor equipped with a magnetically driven stirrer operated at 125 rpm. The stirrer had a special design such as to obtain good mixing; under these conditions no external diffusion limitations were found. To investigate the possibility of internal diffusion limitation, experiments were carried out decreasing the catalyst particle size up to ¼ of the original length. No modifications in activity or selectivity were detected, thus neglecting the existence of internal diffusion limitation. The inner wall of the reactor was completely coated with Teflon in order to avoid the catalytic action of the steel of the reactor found by other authors [3]. The reaction was carried out at 373 K and at 2 MPa constant hydrogen pressure using a volume of liquid of 200 mL and different methanol:benzene ratios (v/v), keeping constant the catalyst weight : benzene ratio. Reactant and products were analyzed chromatographically, using a flame ionization detector and a CP – Wax 52 CB capillary column.

RESULTS AND DISCUSSION

The catalyst contained 4 % Ru and the Ru dispersion was 5 %.

The TPR profile of the unreduced catalyst [7] presents a peak with a maximum at 470 K and a shoulder at about 427 K that can be attributed to the reduction of ruthenium oxide and ruthenium oxychloride, respectively [8].

The XPS characterization of the reduced catalyst [7] indicates the presence of $Ru°$ (Ru $3d_{5/2}$ at 279.7 eV) and of $Ru^{\delta+}$ (Ru $3d_{5/2}$ at 281.1 eV) and chlorine (Cl 2p at 199.0 eV). Hence, chlorine is present after the calcination and reduction steps.

Table 1 presents the total conversion values at 120 min on stream for different methanol:benzene ratios. It can be seen that the highest conversion is reached when methanol is not present.

Table 1

Total conversion, X_T, at 120 min on stream for different methanol: benzene ratios

Methanol:benzene (v/v)	X_T (%)
0	10.8
0.1	9.5
0.3	8.8
1.0	2.8
3.0	2.5

Figure 1 shows the conversion to cyclohexene as a function of time, indicating that the highest conversion is obtained for a methanol:benzene ratio 0.1. Figure 2 presents the conversion to cyclohexene as a function of total conversion for different methanol:benzene ratios, where it can also be seen that the optimum ratio is 0.1.

Finally, Fig. 3 shows the effect of methanol addition on the conversion to cyclohexene; it is noticeable that the conversion to cyclohexene exhibits a maximum for a methanol:benzene ratio 0.1 and then it is decreasing.

From the previous results it is apparent that methanol addition to the reactants increases the conversion to cyclohexene and decreases the total conversion. According to the literature [4], the effect of alcohols in selective hydrogenations is due to an adsorbate-adsorbate interaction between alkene and alcohol. Methanol interacts with a double but not with a single bond and thus interacts with cyclohexene but not with cyclohexane. Besides, methanol cannot interact with benzene because of its delocalized π-system. A hydrogen bond
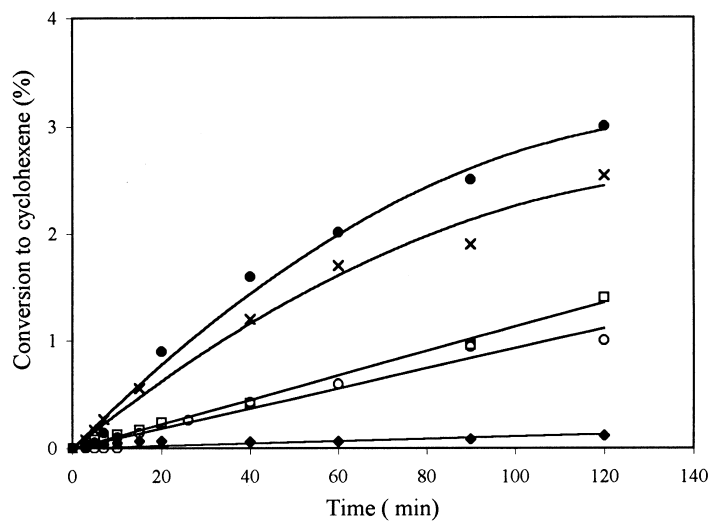
Fig. 1. Conversion of cyclohexene as a function of time for different methanol:benzene ratios: (♦), 0; (•), 0.1; (x), 0.3; (□), 1.0; (o), 3.0
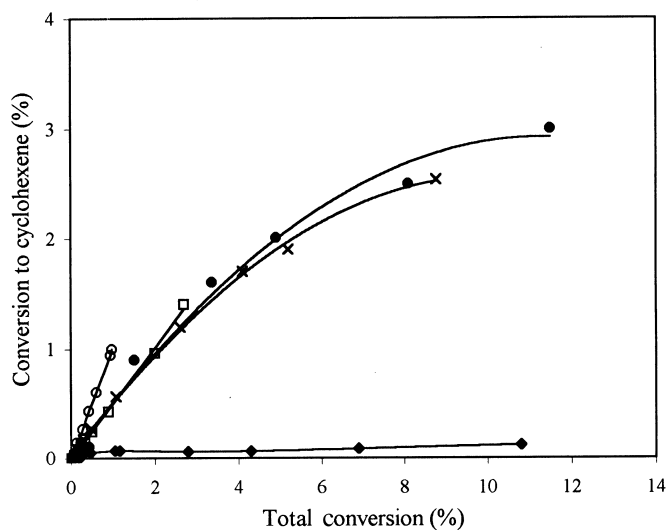

Fig. 2. Conversion of cyclohexene *vs* total conversion for different methanol:benzene ratios: : (♦), 0; (•), 0.1; (x), 0.3; (□), 1.0; (o), 3.0

could be formed between cyclohexene and methanol molecules adsorbed on ruthenium sites, as reported in the literature from FTIR studies [9,10]. Due to the formation of a hydrogen bond, the overlap of the π electrons of cyclohexene double bond with ruthenium d orbitals decreases. Moreover, the methanol-cyclohexene bond is weak (enthalpy of hydrogen bond: -3.75 ± 0.40 kJ mol^{-1} [4]), and this can induce a quicker desorption of cyclohexene bonded to methanol than when cyclohexene is directly bonded to a ruthenium site. The adsorbate-adsorbate interaction increases the conversion to cyclohexene. But this hypothesis cannot explain the existence of an optimum methanol concentration for the conversion to cyclohexene.
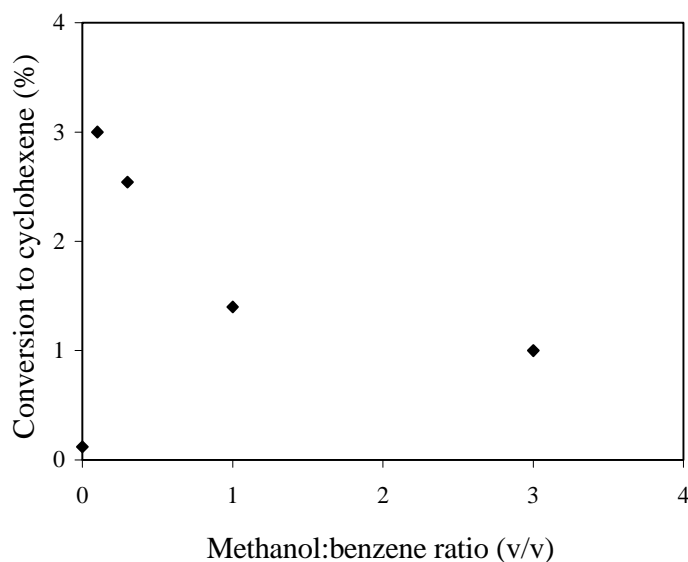

Fig. 3. Conversion to cyclohexene as a function of the methanol to benzene ratio

The positive effect of methanol in the conversion to cyclohexene can also be explained considering a preferential adsorption of methanol on strong ruthenium hydrogenating sites, leaving the weakest hydrogenating sites for benzene hydrogenation [4], thus decreasing the total conversion as we have observed. This hypothesis could better explain our results because we have also found an optimum methanol:benzene ratio of 0.1 for the conversion to cyclohexene. For higher ratios both the conversion to cyclohexene as well as total conversion decrease, suggesting that methanol is also adsorbed on weaker hydrogenating sites in the last case. The existence of hydrogenation sites of

different strengths can be explained from our XPS results: the catalyst has not only Ru° but also electron-deficient Ru species, which can be ascribed to the chlorine remaining in the catalyst.

CONCLUSIONS

Chlorine is present after the calcination and reduction steps in catalysts prepared using ruthenium chloride as precursor. XPS indicates the presence of electron-deficient ruthenium species as well as Ru°.

Methanol addition to the reaction decreases the total conversion; there exists an optimum concentration for the conversion to cyclohexene. The effect can be explained considering that methanol is selectively adsorbed on the most active hydrogenating ruthenium sites (competing with benzene for hydrogenation sites).

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