PROMOTING EFFECTS OF ALKALINE CATIONS ON THE Pd/Y CATALYZED METHYLCYCLOPENTANE CONVERSION

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The conversion of methylcyclopentane over Pd/MY zeolites has been studied with catalysts containing Li, Na or K as charge compensating ions M. It is found that in the sequence M = Li, Na, K the activity for ring opening increases, while that for ring enlargement decreases and the benzene/cyclohexane ratio in the ring enlargement product increases. It is proposed that in the sequence M = Li, Na, K the acid strength of zeolite protons is lowered while electron transfer from donor sites to palladium clusters increases from Li to K.

1. Introduction

The interactions of zeolite encaged transition metals with other metals or cations or zeolite protons have been reported to affect the catalytic performance of the metal particles [1–5]. It was found, e.g. that the presence of unreduced ions of Fe or Cr increases the dispersion stability of Pt or Rh by “chemical anchoring”; the interaction of reduced Pt, Pd or Rh particles with Fe or Cr ions has been detected by EXAFS and Mössbauer spectra [1–4].

Strong electron acceptors have been found to modify the electronic structure of small metal clusters in acidic zeolite cages. Platinum particles, e.g. acquire an electrophilic character [6] owing to partial electron transfer to the modifier. This “electron-deficient” metal exhibits an anomalously high specific activity for hydrogenation and isomerization [7]. Palladium supported on zeolite Y exhibits a similar behaviour [8]. The “superactivity” of Pd in Y zeolite for neopentane conversion has been attributed to a chemical interaction of zeolite protons with reduced Pd particles, resulting in electron-deficient $(Pd_n - H_x)^{x+}$ particles [5].

Much less attention has been given to the interaction of transition metals with basic or electron-donor sites in zeolites. It is anticipated that such basic sites are also able to modify the reducibility and the adsorptive and catalytic properties of encaged transition metals. It has been shown that alkaline cations strongly affect the dimerization rate of ethylene over NiX and PdY zeolites [9]. The enhanced olefin selectivity caused by basic promotors in conventional Fischer-Tropsch catalysts [10] suggests that metal interaction with basic or electron-donor sites might also exert an important influence on the selectivity of hydrocarbon conversion in zeolites. In the present study, the influence of alkaline cations exchanged in Y zeolite on the catalytic behavior of palladium in methylcyclopentane (MCP) conversion was investigated and attention was focused on the influence of electronic interaction between metal and support on specific activities and product distribution.

2. Experimental

A series of Y zeolites was prepared containing as charge compensating cations with either only Na^+ or Li^+ or K^+ in combination with some Na^+. Palladium was subsequently introduced by partial ion exchange with an aqueous solution of $Pd(NH_3)_4(NO_3)_2$. All samples were calcined under pure O_2 at 500 °C for 2 h and then reduced with pure H_2 at 350 °C or 275 °C. These catalysts should, strictly speaking, be referred to as Pd/LiNaHY, Pd/NaHY, or Pd/ KNaHY, since the reduction of Pd^{2+} by H_2 results in the formation of a stoichiometric quantity of H^+ which exhibits strong Brønsted acidity. However, in this paper a short-hand terminology will be used, referring to these samples as Pd/LiY, Pd/NaY, and Pd/KY, respectively. All Pd containing samples have the same Pd loading of wt5% or 8 Pd^{2+} ions per unit cell.

After reduction, the samples were cooled under a H_2 flow to the reaction temperature. The MCP reaction was carried out on 200 mg of the appropriate catalyst in a continuous-flow microreactor at atmospheric pressure, 275 °C, with a H_2/MCP ratio of about 16. The reaction mixtures were obtained by passing purified H_2 through an MCP saturator cooled to 0 °C by an ice/water bath. The reaction flow rates were held constant at 20 ml/min. Reaction products were analyzed by an on-line HP 5794 gas chromatograph with a 50 m crosslinked methylsilicone fused capillary column equipped with FID detector.

3. Results

Figure 1A gives the total MCP conversion vs. time on stream for Pd/Y catalysts containing different alkaline cations. The total activities decrease with time, the sequence of the initial activities is

$$Pd/KY > Pd/NaY > Pd/LiY.$$

The MCP conversion is described as a linear combination of three reactions:

1) Ring opening(RO), i.e. MCP conversion to n-hexane and isohexanes;
2) Ring enlargement(RE), i.e. MCP conversion to cyclohexane and benzene;

3) Cracking, i.e. production of molecules containing less than six carbon atoms.

Since cracking amounts to $< 5\%$ in all cases studied, we shall focus attention on RO and RE.

Figures 1B and 1C show the conversions and the rates of formation of RO and RE products, respectively. It is found that the RO rates reflecting the initial catalyst activities decrease in the order: Pd/KY > Pd/NaY > Pd/LiY; while the RE rates display the opposite sequence, i.e. Pd/LiY > Pd/NaY > Pd/KY. When the catalysts are reduced at a different temperature (350 °C or 275 °C), the activities change, but the selectively sequence remains the same.

When considering the distribution of the RE products, the benzene/cyclohexane ratio is found to increase when part of the Na^+ ions in the zeolite

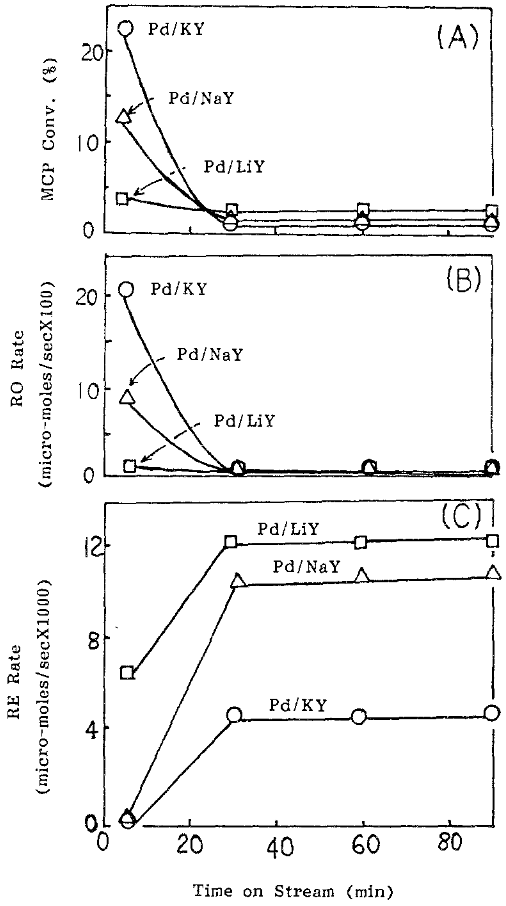

Fig. 1. The effects of alkaline cations on the activity and selectivity of Pd/Y catalysts for MCP reaction. (A). Total conversion of MCP; (B). Rate of ring opening production; (C). Rate of ring enlargement production. Calcination temperature: 500 °C; Reduction temperature: 350 °C; Reaction temperature: 275 °C;

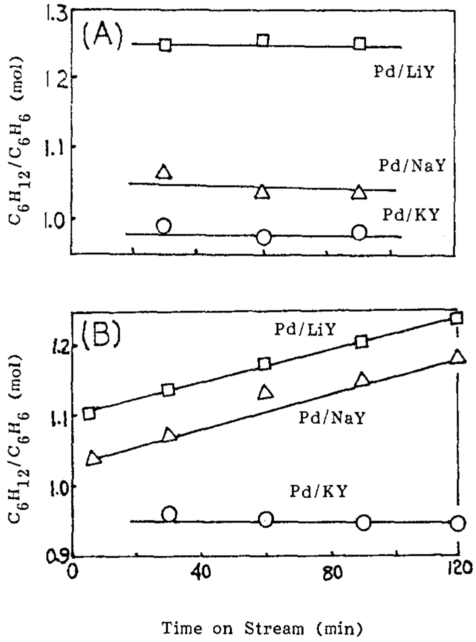

Fig. 2. The effect of alkaline cations on the product distribution of ring enlargement of MCP over Pd/Y. Calcination temperature: 500 °C; Reduction temperature: (A). 350 °C, (B). 275 °C; Reaction temperature: 275 °C.

are replaced by K^+ ions, while this ratio decreases upon partial replacing of Na^+ by Li^+ ions, as shown in figs. 2A and 2B.

4. Discussion

It has been shown by Dalla Betta and Boudart [7] that PtY zeolites containing multivalent cations is 40 times more active towards hydrogenolysis of neopentane than Pt on amorphous supports. They attributed this superactivity to the electron-deficient character of Pt particles. Gallezot et al. [11] found that the extent of electron deficiency of zeolite supported metals increases with the acidity of the zeolite. This is proposed to be due to an interaction of Pt particles with acidic sites, resulting in an electronic charge transfer from Pt to the acidic sites. This hypothesis was evidenced by a shift of the infrared frequency of CO adsorbed on Pt, with acidity of the zeolite support. This kind of shift is usually attributed to a reduced availability of electrons in metal particles to participate in backbonding to the anti-bonding orbitals of chemisorbed CO [12].

There is also evidence that an electron transfer in the opposite direction can occur between metal particles and zeolite supports; also, this transfer will have catalytic consequences. Barthomeuf et al. [13] measured I.R. spectra of adsorbed

CO on Pt in faujasites of different acidity and basicity. They found that the bond due to linear CO is shifted to low wavenumbers as the zeolite acidity decreases and the basicity increases, starting from 2063 cm^{-1} for PtHY, it reaches 2030 cm^{-1} for PtNaX, a value lower than that obtained for Pt supported on a neutral support. These results suggest an electron transfer from Pt to zeolite sites in acidic materials, but from zeolite to Pt in basic samples.

RO of MCP is specific for the metal function in bifunctional catalysts [14]. The results in fig. 1B show, however, that the activity of palladium for RO increases with increasing zeolite basicity from Pd/LiY to Pd/KY. Pd/KY is 20 times more active than Pd/LiY for this reaction. Previously, Homeyer et al. [15] had found that the activity of Pd/SiO_2 or Pd/NaY for RO of MCP increases with decreasing concentration and acidic strength of the protons present on the support. This trend agrees with the present result, showing an increase in RO activity of palladium with increasing basicity of the charge compensating ions. It is, therefore, proposed that MCP ring opening activity is positively related with increasing electron density of Pd. This trend is opposite to that found earlier for neopentane conversion; the activity for that metal catalyzed reaction had been found to increase with electron deficiency of the metal.

Oxygen anions bound to aluminum cations $(AlO_4)^-$ have been proposed [16] as basic sites in alkaline metal exchanged zeolites. The extent to which the negative charge is shielded by the alkaline metal cation decreases as the size of the cation increases and its charge density decreases. The electron-donor strength of the zeolite and, hence, the electron concentration in the supported Pd, is therefore expected to increase in the direction LiY < NaY < KY.

Ring enlargement of MCP, unlike ring opening, is a bifunctional reaction which requires both metal and acidic sites [17]. As shown in figs. 1B and 1C, along which declining RO, RE becomes prevailing. RO, being a hydrogenolysis reaction, is ensemble sensitive and the number of suitable ensembles decreases with time on stream, due to site blocking by coke. RE is a multi-step process, involving acid and metal sites; in RE the latter sites are, however, used only in (de-)hydrogenation steps which are well known to be little ensemble-specific.

Previous work of this lab it had shown that the RE probes specifically for the acidic sites in Pt/NaY and Pd/NaY, that are formed by reduction of the ion exchanged metals [17,18]. Another highly sensitive test for acid sites in Pd/NaY is temperature programmed oxidation (TPO) of the carbonaceous deposits that are formed on the catalyst after MCP conversion. The TPO profile shows two peaks, the lower temperature peak is characteristic for "coke" on the Pd particles, the higher temperature TPO peak characterizes "coke" formed via carbenium ion reactions on Brønsted acid sites. In a recent paper we showed that for reduced Pd/NaY after MCP conversion the TPO peak due to coke on acid sites prevails; however for samples in which the zeolite protons had been neutralized prior to the MCP conversion reaction, this high temperature TPO peak was absent [15]. This TPO peak of acidic coke correlates well with the RE selectivity of the MCP reaction. These results, therefore, justify the use of the RE selectivity as a yardstick for the concentration of protons with strong Brønsted acidity in the hydrogen reduced Pd/NaY samples.

The results in fig. 1C show that the ring enlargement selectivity of the Pd/Y samples containing different alkali ions decreases in the sequence: Pd/LiY > Pd/NaY > Pd/KY. This indicates that the cations affect the acid strength of the protons.

The results in figs. 2A and 2B show that the alkaline cations affect not only the role of ring enlargement, but also the ring enlargement product distribution. The benzene/cyclohexane ratio increases with increasing zeolite basicity from Pd/LiY to Pd/KY. This ratio even becomes > 1 on Pd/KY catalyst.

Besoukhanova et al. [19] have prepared 5 wt% (and 0.6 wt%) Pt catalysts impregnated on L-zeolites, previously exchanged with alkaline ions (Li^+, Na^+, Rb^+ or Cs^+). Studying the n-hexane reaction over these catalysts, they observed that an increase in the basicity of the zeolite, by going from the Li-exchanged to the Cs-exchanged zeolite, caused a corresponding increase in the selectivity towards aromatization. It is tempting to relate this result to the present finding that the benzene/cyclohexane ratio in the RE product increase from Pd/LiY to Pd/KY. One might speculate that an increased electron concentration in Pd lowers the heat of adsorption of benzene, thus facilitating the desorption of this molecule.

5. Conclusions

The MCP conversion over Pd/Y catalysts is significantly affected by the nature of the charge compensating cations. The rate of catalyst deactivation and the intrinsic rates of parallel and consecutive reactions are affected. The observations are rationalized by accepting two effects:

(1). The acid strength of the protons which are formed during reduction of Pd^{2+} ions with H_2, decreases with increasing basicity of the cations. This lowers the rate of the acid catalyzed step in RE.

(2). Electron donation increases the electron concentration in small Pd clusters; this donation is stronger for K than for Li. The metal catalyzed RO of MCP and the metal catalyzed (de-)hydrogenation steps in RE are responding to this with an enhanced rate of RO and an increased benzene/cyclohexane ratio in the RE product respectively.

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