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Influence of pretreatment conditions on acidity of cobalt-based bimetallic systems in NaY zeolite

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Co/NaY, Pt/NaY, Ru/NaY, Ru–Co/NaY and Pt–Co/NaY samples were pretreated in different ways and their Brønsted and Lewis acidities were measured by means of pyridine adsorption and by double-bond isomerization of 1-butene. It is established that during nitrogen/hydrogen pretreatment small metal or bimetallic particles are formed and the system possesses Brønsted and Lewis acidity, whereas by pretreatment in oxygen/hydrogen only Lewis acidity is developed (large metal particles segregated to the zeolite surface). The difference is due to the formation of proton–metal adducts inside the zeolite supercage when nitrogen/hydrogen pretreatment is applied and this is ceased when oxygen/hydrogen pretreatment is used. This is fully supported by the double-bond isomerization of 1-butene to cis- and trans 2-butenes.

Keywords: cobalt-based mono- and bimetallic samples, effect of treatment on Brønsted and Lewis acidity

1. Introduction

It is well known that metal ions inserted into NaY cages can be reduced in a stream of hydrogen and that after reduction the cations are replaced by protons [1]. Furthermore, it has been also proven by several methods [2–5] that e.g. in the case of palladium proton–palladium adducts are formed by which the presence of highly dispersed metal clusters inside the zeolite cage can be stabilized. The presence of protons has also been supported in the CO hydrogenation when during methanol formation in the very first steps no methanol, but dimethyl ether is present and after poisoning of Brønsted acid sites by carbonaceous deposits the DME formation drastically diminishes [6].

Cobalt, platinum and ruthenium and their bimetallic combinations prepared by ion-exchange in NaY zeolite followed by reduction proved to be active catalysts in the CO hydrogenation and also in the low-temperature activation of methane [7,8]. The structure of catalysts and the catalytic behavior of these samples are strongly influenced by the degree of ion-exchange and the catalyst pretreatment conditions. In the present article the influence of pretreatment on the acidity of bimetallic zeolite catalysts is presented.

2. Experimental

Samples

The Co/NaY, Pt/NaY and Ru/NaY samples were prepared by sequential ion-exchange of NaY in solutions of $Co(NO_3)_2$, $Pt(NH_3)_4Cl_2$ and $Ru(NH_3)_6Cl_3$, respectively, at 333 K. For producing Co–Pt/NaY and Co–Ru/NaY samples NaY was ion-exchanged first for Pt^{2+} or Ru^{3+} ions followed by introduction of Co^{2+}. The samples were analyzed by XRF and characterized by XRD, IR, TPD and XPS methods [9–12].

Acidity measurement

For acidity determination pyridine adsorption monitored by FTIR spectroscopy was used. From the powdered zeolites, self-supported wafers were pressed with a thickness of 10 mg/cm^2. The wafers, placed into a sample holder made of glass, were pretreated in three different ways.

Pretreatment 1

The sample was heated in flowing oxygen (40 cm^3/min) up to 573 K using 0.5 K/min ramp and kept at this temperature for 2 h followed by flushing in nitrogen (30 cm^3/min) for 30 min. Then the sample was evacuated for 30 min and cooled to room temperature where the spectra of activated zeolites were taken and the pyridine loading was performed.

Pretreatment 2

The oxygen-treated sample (see above) was flushed with nitrogen and the temperature of the cell was raised to 673 K followed by switching the nitrogen stream to a hydrogen one. The reduction was performed for 2 h for each sample. The cell was then evacuated and cooled down to room temperature and the spectra of the activated samples were recorded followed by measuring infrared spectra after pyridine adsorption.

Pretreatment 3

For the ruthenium-containing samples the wafers were slowly (0.5 K/min) heated to 673 K in flowing nitrogen (30 cm^3/min) and kept at this temperature for 2 h. Then the nitrogen stream was changed for hydrogen at the same temperature and the reduction was carried out for 2 h followed by evacuation and cooling to room temperature for pyridine adsorption, which was performed after taking the spectra of the activated zeolites.

Experimental procedure

1.33 kPa of pyridine was loaded to the wafers at room temperature followed by increasing the temperature of the cell to 473 K. The adsorption was performed at 473 K for 2 h followed by evacuation of the excess and physisorbed pyridine at the same temperature. After cooling to ambient temperature the spectrum of the adsorbed pyridine was recorded. The integrated absorbances divided by the mass of the wafer were regarded as measure of zeolite acidity.

A Mattson Genesis I FTIR spectrometer with 2 cm^{-1} resolution was used for spectroscopic measurements. 1-butene double-bond isomerization was used as test reaction. For catalytic measurements an all glass made circulation system on line connected to a Varian 1400 type gas chromatograph was applied.

3. Results and discussion

3.1. Acidity measurements

Metal loading determined by XRF analysis was 5.6, 10.2 and 4.1 wt% for Co/NaY, Pt/NaY and Ru/NaY samples, respectively. The metal contents of Co and Pt for the Co–Pt/NaY sample are 2.4 and 10.3 wt%, respectively and those for Co–Ru/NaY 2.8 and 3.8 wt%. No structural change due to the sample preparation was detected either by XRD or FTIR techniques.

Fig. 1A shows the IR spectra of pyridine adsorbed on Co/NaY after pretreatments 1 and 2. The IR bands appeared in the regions characteristic of both the Brønsted and the Lewis acidities, 1540 and 1450 cm^{-1}, respectively. In the spectrum of the sample pretreated in oxygen only, two Lewis bonded pyridine bands are observed. This is likely due to the presence of Co^{2+} ions and the cobalt oxide formed upon the oxidative treatment. In the spectrum of pyridine adsorbed on the sample pretreated in reductive atmosphere only one Brønsted and one Lewis bonded pyridine band are seen. An increase in the concentration of Brønsted acid sites would be expected after reductive treatment, however, the cobalt ions cannot be easily reduced. If some more Brønsted acid sites formed upon reduction, they should be dehydroxylated due to their low thermal stability. Since the reduction of cobalt ions and thereby formation of the Brønsted acid sites is restricted, the mentioned increase actually could not be observed (the spectrum was recorded on a sample pretreated at 673 K in vacuum, thus, the probability of dehydroxylation was enhanced).

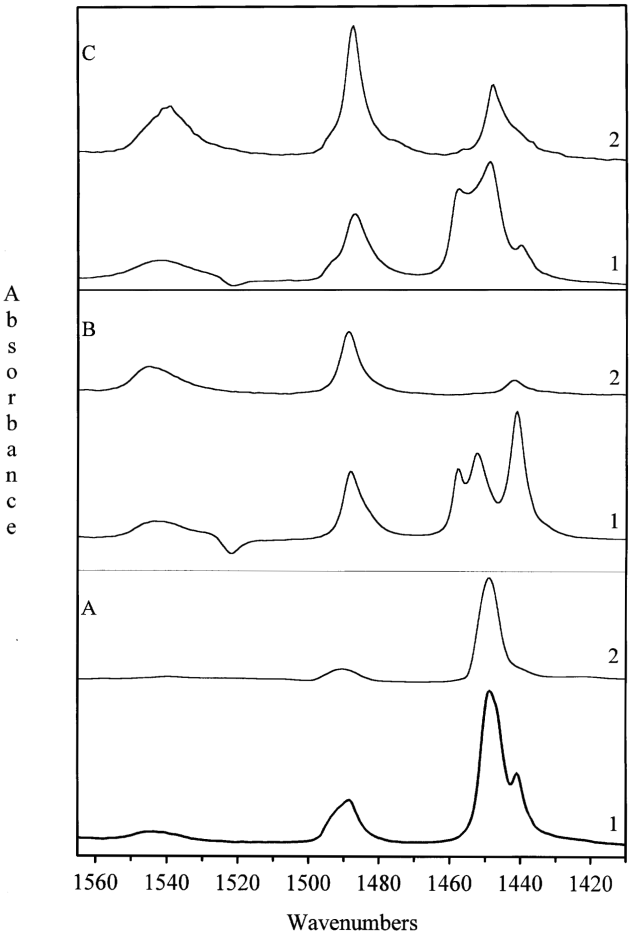

Fig. 1. FTIR spectra of pyridine adsorbed on Co/NaY (A), Pt/NaY (B) and Pt–Co/NaY (C) samples measured after pretreatment in oxygen (1) and in oxygen/hydrogen (2).

In fig. 1B, the IR spectra of the pyridine adsorbed on Pt/NaY zeolite pretreated in different ways are presented. In the spectrum taken after pretreatment in oxidative conditions (pretreatment 1) a weak Brønsted bonded pyridine band appeared. In contrast, the band characteristic of the Lewis acid site bonded pyridine is rather complex. Three intensive bands can be distinguished in this region and assigned to platinum ions in different crystallographic and chemical environments. The spectrum taken after reductive pretreatment is much simpler and two bands can be observed. The band due to the Brønsted bonded pyridine is much more intense than that characteristic of the Lewis acid sites. The increased Brønsted acidity is explained by the easy reduction of platinum ions to metallic platinum. It should be noted that 673 K was applied for reduction and under this condition all platinum ions are transformed to metallic particles.

After oxidative treatment the spectrum of the

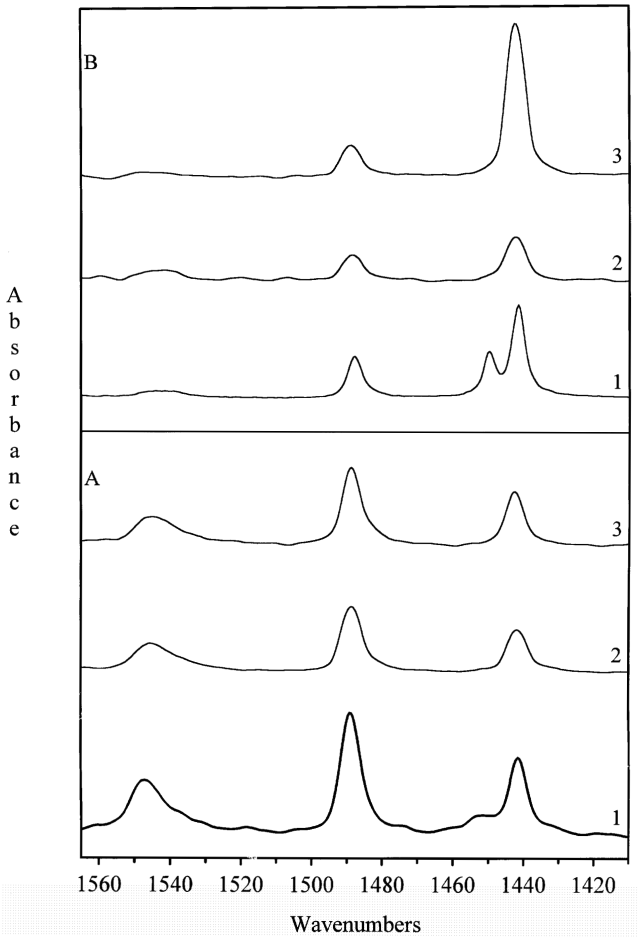

Fig. 2. FTIR spectra of pyridine adsorbed on Ru/NaY (A) and Ru–Co/NaY (B) samples measured after pretreatment in oxygen (1), in nitrogen/hydrogen (2) and in oxygen/hydrogen (3).

adsorbed pyridine on the Pt–Co/NaY sample was similar to that on the Pt/NaY sample treated in the same way. Here the relative amount of Lewis acid sites decreased compared to the Co/NaY, however, the Brønsted acidity increased to a very small extent and became almost equal to the value measured on Pt/NaY. The reductive treatment diminished the number of Lewis acid sites and enhanced the number of Brønsted acid sites, which is illustrated in fig. 1C.

Fig. 2A shows the IR spectra of pyridine after adsorption on Ru/NaY zeolite using pretreatment procedures 1, 2 and 3. No significant change in the spectra was recorded after these treatments. Each spectrum shows the Brønsted and the Lewis bonded pyridine bands.

The Ru–Co/NaY sample, upon oxidative treatment, displayed a Lewis acidity higher than was measured on Ru/NaY. The oxidative treatment caused a decrease in the concentration of Brønsted acidity as shown in spectrum 2 in fig. 2B. On the sample pretreated in nitrogen as inert gas followed by reduction at 673 K a lower amount of Lewis acidity was detected, although two distinct Lewis site bonded pyridine bands could be observed.

The integrated absorbances are summarized in table 1.

3.2. Kinetic measurements

1-butene double-bond isomerization is a measure of the Brønsted acidity, thus, it can be applied to support the result measured by pyridine adsorption. In fig. 3 the kinetic curves of 1-butene decomposition and cis- and trans-2-butene formation are presented. On the Ru–Co/NaY sample treated in nitrogen followed by hydrogen reduction at 673 K, the isomerization of 1-butene easily takes place at 298 K in the absence of hydrogen. On the other hand, the sample treated first in oxygen at 573 K followed by reduction in hydrogen at 673 K shows no activity at all.

Not only our works [8,12], but other studies also indicated that when ruthenium is not treated in oxygen before hydrogenation the ruthenium particles are located in the supercages and the size is not bigger than that of the supercage. Careful studies have shown that the size is really around 1 nm in most cases illustrated by TEM and chemisorption studies [13–17]. Brønsted acidity exists only when small metal particles are located in the supercage of NaY which gives further evidence for the existence of a metal–proton adduct linked to the zeolite framework oxygen ions. However, if, during oxygen treatment, most of the metal particles migrate towards the external surface, the hydrogen is probably replaced by other cations, such as AlO^+ formed through partial dealumination of the zeolite framework, can be a source for charge compensating cations [18]; thereby the sample loses its Brønsted acidity. In the Pt–Co/NaY system the change of sodium concentration during pretreatment has also been monitored by means of XPS and indeed,

Table 1
Integrated absorbances of the IR bands of pyridine bound to the Brønsted (B) and the Lewis (L) acidic sites

Samples	O_2/N_2		O_2/H_2		N_2/H_2	
	B	L	B	L	B	L
Ru	0.42	0.42	0.22	0.29	0.27	0.26
RuCo	0.20	0.96	0.06	0.78	0.11	0.32
Co	0.24	2.55	0.02	0.93	–	–
Pt	0.31	1.39	0.36	0.13	–	–
PtCo	0.29	1.44	0.57	0.55	–	–

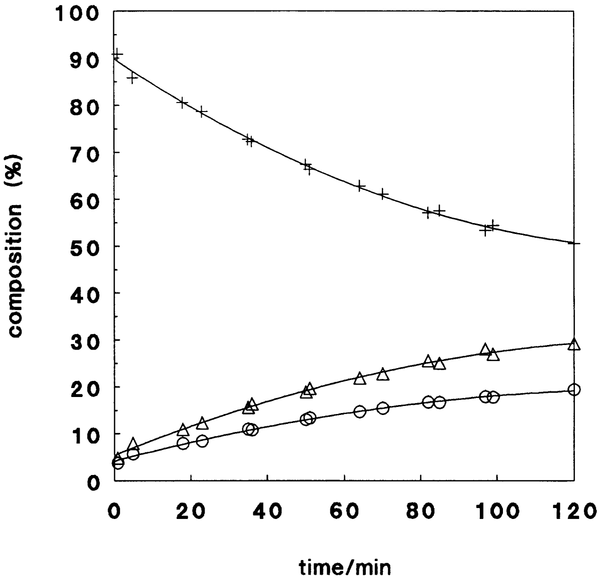

Fig. 3. Double-bond isomerization of 1-butene into cis- and trans-2-butene at 298 K, in 133 kPa 1-butene over Ru–Co/NaY sample treated in nitrogen/hydrogen at 573/673 K. On Ru–Co/NaY samples treated in oxygen/hydrogen the conversion was nil. (+) 1-butene, (△) trans-butene, (○) cis-butene.

some dealumination was also measured [19]. These results also support the observation that, after cleavage of proton–small metal particle adduct, anions in the zeolite framework are being compensated by the various cations in the vicinity. This results in the decrease of Brønsted acidity we observed.

4. Summary

Bimetallic catalysts prepared by sequential ion-exchange in NaY show Brønsted and Lewis acidity. The former is very sensitive to the small metal particles encaged inside the zeolite supercage via metal–proton adducts. The determining role of pretreatment conditions on the acidic behavior of zeolites was proven.

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