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XPS Study of Nickel in NiHZSM5 Catalysts[1]

Hydrogen-exchanged ZSM5 zeolites (HZSM5) are active catalysts in a wide variety of processes involving the formation or transformation of alkylaromatic hydrocarbons (*1*). The production of *para*-xylene from a mixture of C_8 alkylaromatic hydrocarbons is one of the processes of commercial importance (*2*). In such isomerization reactions over acidic catalysts, small quantities of transition metal ions, like platinum, palladium, or nickel are usually added to the catalyst to prolong its active life. What is the structural role of the transition metal in such cases? The presence of metal ions may influence the Brønsted acid sites in zeolites (*3*). A second consequence is that the metal cation itself may modify the catalytic activity (*4*). Yet another consequence can be that in the presence of hydrogen at elevated temperatures, the transition metal ions are reduced to the metallic state. They can, then, hydrogenate the unsaturated coke precursors and suppress the formation of coke on the catalyst surface, thereby prolonging the active life of the catalyst. While the last explanation may be valid in the case of platinum and palladium, it cannot be generalized to include the case of nickel also, especially in view of the difficulty in reducing Ni^{2+} to Ni^0 when nickel is supported on acidic catalysts (*5–7*). Wu and Hercules (*5*), for example, found that at low nickel content, nickel in nickel–alumina was not reduced easily to the metallic state. The ease of reduction was found to depend on the type of support, metal loading, and final calcination temperatures. Similarly, Minchev *et al.* (*6*) found that a large fraction of nickel in NiY zeolite was not reduced to the metallic state in H_2.

In the present study we report the XPS study of nickel in a NiHZSM5 (0.7 wt% Ni) catalyst used for the isomerization of xylenes. It was found that the presence of nickel suppressed catalyst aging significantly (Fig. 1) (*8*). The objective of the present study is to characterize the oxidation state of nickel in such a catalyst, especially under operating conditions.

Sample A was NiHZSM5 (0.7 wt% Ni, $SiO_2/Al_2O_3 = 86$) prepared from NH_4ZSM5 by ion exchange with nickel nitrate solution followed by drying and calcination in air at 383 and 823 K, respectively. Sample A was utilized in a pilot plant for the isomerization of *o*-xylene to a mixture of the three isomeric xylenes at 673 K, LHSV = 6, H_2/*o*-xylene = 2 and pressure = 10 bars, for more than 10 days. At the end of 10 days, the catalyst was still fully active. It was, then, freed of adsorbed hydrocarbon molecules by purging with pure hydrogen at 673 K, and then unloaded for XPS study. This used catalyst is designated as sample B. Samples C, D, E, and F were prepared by the reduction of sample A in pure hydrogen *in situ* in the electron spectrometer for 2 hr at 523, 573, 673, and 733 K, respectively. After each reduction process, the sample was transferred from the preparation to the analyzer chamber of the spectrometer for scanning the spectra.

The XPS measurements were performed with a commercial XPS spectrometer (Vacuum Generators, ESCA 3 Mk II) A Mg$K\alpha$, X-ray source ($h\nu = 1253.6$ eV) was used. A slit width of 4 mm and analyzer energy of 50 eV were used. The spectrometer chamber was separated from the preparation cham-

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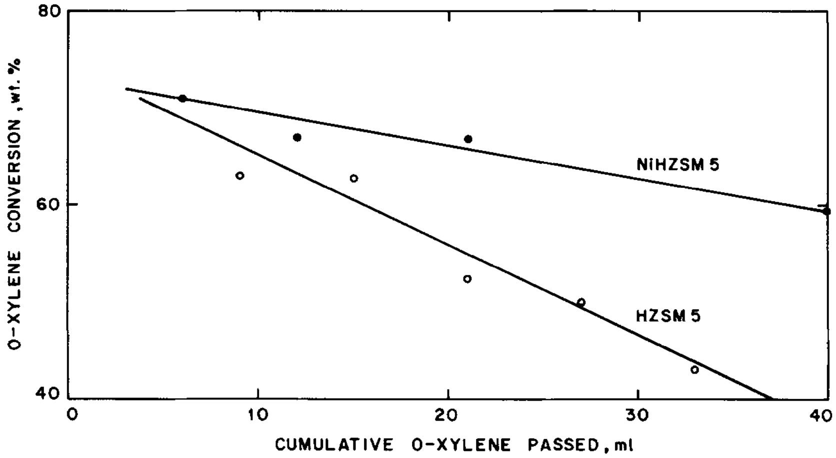

FIG. 1. Influence of nickel on catalyst aging. Reaction conditions: Pressure = 1 bar; Temp. = 608 K; LHSV = 6; Hydrogen/*o*-xylene = 2. The catalysts were used in the form of particles (10–22 mesh).

ber by a Viton-sealed valve. The samples were mounted on a probe which could be heated up to 873 K in various atmospheres and then evacuated and transferred to the analyzer chamber without exposure to air.

A binding energy of 103.3 eV for the Si_{2p} level was used as the internal standard for all the samples. The accuracy of the binding energies as determined with respect to this standard value was within 0.2 eV. The binding energy and FWHM (full width at half maximum) values of O_{1s} and Ni_{2p} determined from the spectra are given in Table 1. The surface Si/Ni atom ratios were calculated by the use of Wagner's (9) sensitivity factors using the relationship

$$\frac{\mathrm{Si}}{\mathrm{Ni}} = \frac{I_{\mathrm{Si}}}{I_{\mathrm{Ni}}} \times \frac{\sigma_{\mathrm{Ni}}}{\sigma_{\mathrm{Si}}} \times \frac{(E_{\mathrm{k_{Si}}})^{1/2}}{(E_{\mathrm{k_{Ni}}})^{1/2}},$$

where I_{Si} and I_{Ni} are the heights of the Si_{2p} and Ni_{2p} peaks, respectively. The σ and E_k values refer to the sensitivity of detection (*9*) and the kinetic energy of the photoelectron, respectively. Peak heights, rather

TABLE 1

XPS Parameters of NiHZSM5 Catalysts

Sample	Si_{2p}		O_{1s}		Ni_{2p}		Si/Ni	Ref.
	B.E.	FWHM	B.E.	FWHM	B.E.	FWHM		
A	103.3	2.4	532.5	2.4	856.5	4.3	3.4	This study
B	103.3	2.8	532.1	2.4	855.9	4.4	1.8	This study
C	103.3	2.4	531.9	2.4	856.3	4.4	3.3	This study
D	103.3	2.4	531.9	2.4	855.7	4.4	3.0	This study
E	103.3	2.4	532.4	2.4	856.1	4.4	3.2	This study
F	103.3	2.4	532.9	2.4	856.5	4.4	3.4	This study
Ni^0					852.6	2.0		*10*
NiO					854.8	4.2		*10*
Ni_2O_3					855.8			*11*
$Ni(OH)_2$					855.6			*11*
$Ni–Al_2O_3$(7%Ni)					856.2	3.6		*5*
NiNaY					856.9	4.0		*12*
HZSM5	103	2.4	532.4	2.4				*13*

than areas, were used (*9*), for the estimation of Si and Ni. The estimated Si/Ni values are also tabulated in Table 1. The XPS parameters of nickel in some reference compounds and in Ni–Al_2O_3 and NiNaY are also given in Table 1 as well as the values for Si_{2p} and O_{1s} in HZSM5 (*13*). The Al_{2p} peak around 74 eV could not be seen in any of our samples, probably due to their low Al content ($SiO_2/Al_2O_3 = 86$).

Both the B.E. and FWHM values for Si_{2p} and O_{1s} levels in our samples agree well with those of Vedrine *et al.* (13) for a sample of HZSM5 (Table 1). Turning our attention to the Ni_{2p} level, the most striking feature is that for all the samples studied both the B.E. and FWHM values remain constant, within experimental errors, implying that the same species of nickel is probably responsible for the Ni_{2p}, XPS spectra in all the samples. In other words, the nickel ions that were present in the fresh, calcined catalyst (Sample A) had not undergone any major chemical modification (like reduction to Ni^0) during use in the pilot plant trial (Sample B) or the various reduction procedures (Samples C–F). The presence of Ni^0 in any of our samples can be ruled out since B.E. and FWHM values reported for Ni^0 (852.6 and 2.0 eV respectively) (*10*) are quite different from those of our samples. Moreover, since Ni^0 is not expected to be present in the catalyst calcined in air at 823 K (Sample A) and the Ni_{2p} spectra is similar in all the samples, the presence of Ni^0 in the other samples is also unlikely.

Since the nickel ions in our samples are not reduced in H_2 even at high temperatures and pressures, the presence of NiO and Ni_2O_3 phase is also unlikely since these oxides are known to be reduced to the metallic phase under these conditions (*11*). The B.E. and FWHM values in our samples are quite similar to those for nickel in NiNaY (*12*) and $Ni(OH)_2$ (*11*). Kim *et al.* (*11*) reported that $Ni(OH)_2$ is not reduced even under Ar^+ bombardment while this treatment reduced NiO and Ni_2O_3 to Ni^0. Even when the nickel content was as high as 7.7 wt% (in NiY), Minchev *et al.* (*6*) found that a remarkable amount of nickel was not reduced in H_2 even at 723 K. Our results suggest that nickel in our NiHZSM5 samples is present as Ni^{2+} ions, probably coordinated to (OH) groups, even during their use in the xylene isomerization process. Hence, its promoting action in prolonging the life of the catalyst (Fig. 1) cannot be ascribed to the presence of metallic nickel.

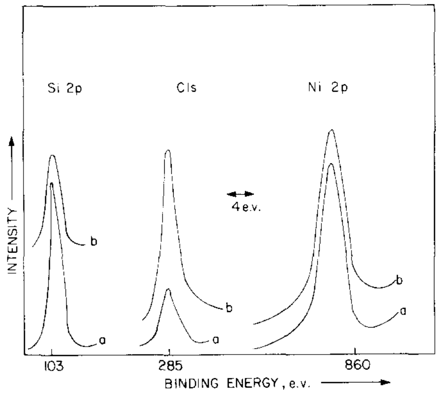

FIG. 2. XPS spectra of NiHZSM5. Curves a and b refer to Samples E and B, respectively.

Further light is thrown on the state of the catalyst during use by the data presented in Fig. 2. The catalyst after use in the isomerization reaction (Sample B) contained about 4 wt% of carbon. It is seen (Fig. 2) that while the absolute intensity of the Ni_{2p} peak is the same in samples B and E, the peak due to Si_{2p} is attenuated in sample B, probably due to the coverage of Si atoms by carbon. This is also reflected in the Si/Ni values (Table 1) of 1.8 and 3.2 for samples B and E, respectively. The nickel ions are, hence not appreciably covered by "coke" during the isomerization process and can serve as adsorption centers for molecules like hydrogen.

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S. BADRINARAYANAN
R. I. HEGDE
I. BALAKRISHNAN
S. B. KULKARNI
P. RATNASAMY[2]

National Chemical Laboratory
Poona 411 008, India

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[2] To whom all correspondence should be addressed.