CHEMISORPTION OF OXYGEN ON SUPPORTED NICKEL CATALYSTS

Hana ZAHRADNÍKOVÁ, Olga ŠOLCOVÁ and Kvĕta JIRÁTOVÁ

Institute of Chemical Process Fundamentals,
Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchdol

One unsupported nickel catalyst and seven nickel catalysts (about 55 wt.% Ni) supported on SiO_2, Al_2O_3, TiO_2, Nb_2O_5, ZrO_2, V_2O_5 and ZnO were characterized by pulse dynamic oxygen chemisorption measured at -78 °C and evaluated in the reaction of reductive amination of diethylene glycol. Correlation was obtained between their oxygen uptake and catalytic activity.

One of the most useful ways of characterizing a supported catalyst is the determination of specific surface area of the catalytically active ingredient. On supported nickel catalysts, hydrogen chemisorption is taken for the most convenient, accurate and generally applicable technique. Hydrogen to nickel atom stoichiometry is 1 : 1, which was proved by measurement of nickel particle size by physical methods[1–3]. However, hydrogen chemisorption is suppressed and the method cannot be used when nickel is in the strong metal–support interaction state (SMSI)[2,4].

Also carbon monooxide and oxygen chemisorption has been applied for characterization of nickel catalysts[1,2,4,5]. While the use of carbon monooxide appears to bring no advantage in comparison with hydrogen[1,5,6,7], further study of oxygen chemisorption seems to be meaningful. According to Hoang-Van et al.[2] and Smith[4], static oxygen chemisorption at ambient temperature can give sufficiently accurate information on nickel dispersion on supported nickel catalysts even at their SMSI state. Also with the catalysts prepared from nickel chloride as an impregnation salt, oxygen chemisorption gave good results while hydrogen chemisorption has failed[2]. The stoichiometry of oxygen chemisorption on nickel is, however, much more complicated than that of hydrogen and various values of O/Ni atom ratio ranging from 1 to 4 have been noticed in the literature[1,2,6,8]. It depends not only on the type and state of the catalyst, but also on experimental conditions of the chemisorption[1]. Kuijpers[9] and Slinkin[10] demonstrated the existence of at least two types of oxygen–nickel bonds on the surface of Ni/SiO_2 catalyst. Smith[4] found that the oxygen to nickel atom ratio changed from 2 : 1 to 1 : 1 when the catalysts got into SMSI state. Similar results were obtained by Hoang-Van et al.[2]. It is worth noting that the O/Ni ratio corresponding to monolayer coverage was found especially on low-loaded nickel catalysts appearing in SMSI state. All other pub-

lished stoichiometry values correspond to the higher oxygen coverage and it is not thus quite clear if additional layers were deposited on the surface or under it. Kuijpers[9] came to the conclusion that a subsurface layer of oxygen is formed at static oxygen chemisorption at ambient temperature, what can possibly turn to bulk oxidation.

Volumetric methods are applied most often for chemisorption measurements as they give the most precise and reproducible results. Nevertheless, the experiments are highly time-consuming and the possibility of subsurface oxidation of nickel exists. These disadvantages can be eliminated by pulse dynamic arrangement of experiments. When practised at appropriate temperature, nonspecific adsorption is surpressed, and at the same time the possibility of bulk oxidation is minimized. Till now, however, dynamic chemisorption of oxygen has not been commonly applied for nickel catalyst characterizations. Only Zielinski[11] employed this method at 0 °C on the Ni/Al$_2$O$_3$ catalyst. Since he did not determine the oxygen to nickel stoichiometry, there is no comparison with the results obtained by static methods. But it is highly probable that both the temperature and the way of measurement can affect the amount of chemisorbed oxygen.

No measurements of oxygen chemisorption on high-loaded nickel catalysts have as yet been done, but Narayanan et al.[12] used chemisorption of hydrogen on the Ni/Al$_2$O$_3$ catalysts loaded up to 50 wt.% of nickel. Also low-loaded nickel catalysts with various extent of metal interaction were studied. Nickel dispersion and reducibility on nickel/Al$_2$O$_3$ catalysts were parallel to the act vity in hydrogenation of benzene. It was found that strong metal–support interaction decreases the reducibility of low-loaded catalysts while on high-loaded catalysts, multiple layers of metal oxides were easily reduced, but agglomerated to form large crystallites with decreasing surface area. Activity of the catalysts was in all cases proportional to the available metal surface area measured by hydrogen chemisorption. From the above study it is not clear whether the strength of metal support interaction still plays a role at very high metal loadings. As regards the oxygen chemisorption on high-loaded nickel catalysts, it seems to be evident that the problem of a surface or subsurface process can be crucial.

In this work we made attempt to verify the use of the low temperature (–78 °C) pulse dynamic measurements of oxygen chemisorption for the characterization of supported high-loaded nickel catalysts. We tried to find a relation between oxygen chemisorption capacity and the activity of the catalysts in the reductive amination of diethylene glycol, which is the reaction performed in practice on high-loaded supported nickel catalysts. We assumed that the correlation between chemisorption capacity and activity in the reaction proceeding on nickel active sites should exist if the oxygen chemisorption under the conditions we used is exclusively a surface process, regardless of the effect of chemisorption conditions on the adsorption stoichiometry.

EXPERIMENTAL

All supported catalysts were prepared by mixing the individual supports (silica, alumina, titania, zirconia, vanadia, niobia, zinc oxide) with the solution of basic nickel carbonate in ammonia[13]. The content of NiO in the catalysts was about 70 wt.%. The same procedure was used for the preparation of unsupported nickel oxide. The catalysts were dried, calcined at 370 °C for 3 h, crushed and screened to 0.16 – 0.315 mm particle size. Surface area of the catalysts was determined with Digisorb 2600 Instrument (Micromeritics, U.S.A.) using BET method.

Oxygen chemisorption measurements were conducted by pulse dynamic method on the apparatus described in details elsewhere[14]. Prior to chemisorption measurements, each catalyst sample was dried in situ for 1 h at 150 °C in a stream of helium. Then it was reduced in hydrogen, temperature of the reduction being gradually increased by 25 °C per hour to the final temperature of 300 °C (or, in some cases, to the higher temperature in the range 350 – 450 °C) at which each sample was reduced for another 2 h. After the reduction, the catalyst was flushed with helium for 1 h at 400 °C, cooled under helium to –78 °C and kept at this temperature for another 1 h. After that, oxygen pulses were introduced into helium stream at one minute intervals and the oxygen uptake was detected by thermal conductivity detector. The volume of chemisorbed oxygen was determined with fairly good reproducibility ±15%.

The activity of the catalysts in the reaction of diethylene glycol with ammonia was measured in the integral flow reactor with fixed catalyst bed at 190 °C and atmospheric pressure. The pseudo-first order rate constants k, l kg^{-1} h^{-1}, for diethylene glycol disappearance related to the unit of catalyst mass were taken as the measure of catalyst activity.

RESULTS AND DISCUSSION

Catalyst compositions, the BET surface areas and oxygen uptake on reduced catalysts are given in Table I. At the approximately equal nickel content and at the same treatment, the catalysts could differ in nickel dispersion due to different properties of the supports at least for two reasons. First, there is a direct effect of the total specific surface area and morphology of the used supporting oxides. Second, there is the effect of different strength of interaction between active nickel phase and the support which affects the dispersion of nickel phase on the support surface during the process of preparation. It is seen from Table I that the total surface area of the unreduced supported catalysts varied from 46 to 172 m^2 g^{-1}.

An additional effect of the strength of interaction can be expected during the process of reduction. Strong interaction of nickel with the support is supposed to decrease its reducibility, but it should lead to the reduced nickel phase well dispersed on the support surface, not tending to sinter too easily. With weak interaction between nickel and the support, good reducibility can be expected, along with the formation of the possibly less dispersed phase of reduced nickel with the smoother surface and tendention to further sintering, accompanied by further surface area decrease. All these facts will presumably take part in formation of resulting nickel specific surface area on the reduced supported catalysts, which is assumed to be measured by hydrogen chemisorption and at least estimated by oxygen chemisorption. It can be seen from Table I that the values of oxygen uptake on the reduced catalysts do not correlate exactly with the total

surface of the unreduced catalysts. Even at very high nickel content, the strength of interaction probably plays a role not only during the preparation, but also during the process of reduction.

In Fig. 1 there are the results of oxygen chemisorption measurements on the catalysts reduced at temperatures higher than 300 °C. The more detailed dependence of oxygen uptake on the reduction temperature was measured for the Ni/SiO_2 catalyst. It is seen

TABLE I
Compositions of the catalysts (assuming complete reduction of NiO), BET surface areas ($m^2 g^{-1}$) and volumes of chemisorbed oxygen V_0 (ml g^{-1}) for the catalysts reduced at various temperatures (300 °C and >300 °C)

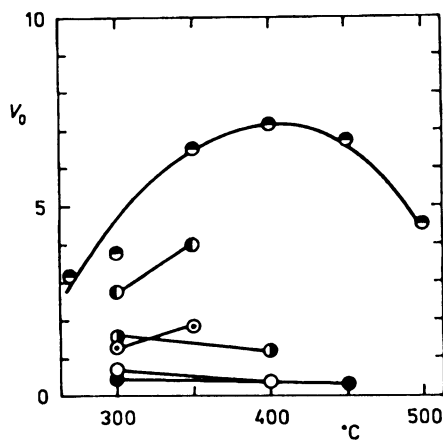| Sample	Support	Ni, wt.%	Surface area	V_0	
				300 °C	>300 °C
1	SiO_2	57	179	3.7	8.1^a
2	Al_2O_3	52	123	2.7	4.0^b
3	TiO_2	54	64	1.2	1.7^b
4	V_2O_5	57	121	–	3.7^a
5	Nb_2O_5	52	46	0.7	0.3^c
6	ZrO_2	58	58	1.5	1.2^c
7	ZnO	52	88	–	1.4^b
8	–	100	89	0.5	0.3^a

^{a} 450 °C; ^{b} 350 °C; ^{c} 400 °C.

FIG. 1
The oxygen uptake V_0 (ml g^{-1}) on the supported nickel catalysts in dependence on the reduction temperature (°C). Type of the supports: ◖ SiO_2, ◗ Al_2O_3, ⊙ TiO_2, ○ Nb_2O_5, ◗ ZrO_2, ● NiO

that in the temperature range 300 – 450 °C oxygen uptake depends on the reduction temperature and goes through a maximum located at about 400 °C. Also for the Ni/Al_2O_3 and Ni/TiO_2 catalysts oxygen uptake observed at 350 °C is higher than that at 300 °C. These three catalysts are reported in literature[2] as those with relatively strong metal–support interactions. From our experiments it is evident that in the examined temperature range no switch to SMSI state (accompanied by a distinct drop in oxygen stoichiometry) proceeds, or, if it does in the active phase layers next to the support surface, it is not detectable by adsorption on the surface layers at the high nickel loadings used. Increase of the oxygen uptake may be explained by the more difficult reducibility of these catalysts[15] caused by the stronger nickel–support interaction (but not necessarily by SMSI state) which is overcome by increase of the temperature of the reduction. The following decrease of oxygen uptake at the Ni/SiO_2 catalyst (which can be assumed at two other catalysts discussed as well) can probably be ascribed to the start of nickel sintering. In the case of the catalysts with very weak nickel–support interaction, oxygen uptake at 400 or 450 °C is lower than that at 300 °C. These catalysts are easily reducible[15] and, due to weak interaction between support and active phase, highly susceptible to sintering. If any maximum of their chemisorption capacity in this temperature range exists, it lies between 300 and 400 °C.

Though we have no information to support any our hypothesis on chemisorption stoichiometry or mechanism, it is very improbable that any migration of oxygen under the catalyst surface could occur at –78 °C and a short contact of oxygen with the surface. (After Kuijpers[9], such a migration proceeds under conditions of static chemisorption at ambient temperature, starting with the change of positions between oxygen atom and the nickel atom under it). On the contrary, it is probable that chemisorption
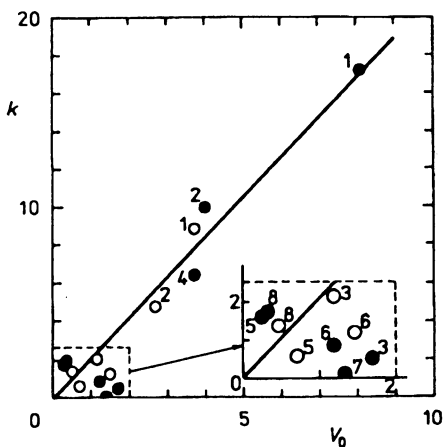

FIG. 2
Correlation of the pseudo-first rate constants of diethylene glycol transformation k (l kg^{-1} h^{-1}) on the oxygen uptake V_0 (ml g^{-1}) for various supported nickel catalysts. Numbers of the catalysts see Table I, blank points denote the reduction temperatures 300 °C, full points the temperature range 350 – 450 °C

proceeds exclusively on the surface and is even more specific than under the conditions of static method at ambient temperature. Monolayer coverage apparently may not be achieved, and the absolute values of oxygen uptake can hardly be compared to values obtained under different conditions. Nevertheless, proportionality to nickel dispersion can be still expected.

The oxygen uptakes found on the reduced catalysts were correlated with the catalyst activities in the reductive amination of diethylene glycol. Roughly linear correlation was obtained in the region of the rate constants higher than approximately 2 l kg^{-1} h^{-1} (Fig. 2). For the catalysts with very low nickel surface area and accordingly the low catalytic activity (as well as chemisorption capacity), the catalyst activity measurements conducted in our experimental arrangement cannot be taken as sufficiently precise and reliable. The data plotted in Fig. 2 are still in accordance with the suggestion that oxygen chemisorption on our high-loaded catalysts reduced in the screened temperature range proceeded exclusively as a surface process, and the values of oxygen uptake are proportional to nickel dispersion.

From the findings of the present work it can be concluded that oxygen chemisorption data obtained by pulse dynamic oxygen chemisorption at −78 °C can serve for the estimation of both nickel dispersion and catalytic activity in appropriate reactions and can be very useful in screening of comparable supported nickel catalysts.

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