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Supported CuO + Ag/Partially Stabilized Zirconia Catalysts for the Selective Catalytic Reduction of NO_x under Lean Burn Conditions

2. Catalytic Properties

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The catalytic performances of copper oxidic species supported on mesoporous zirconia supports stabilized by alkaline earth cations were studied for the reactions of NO oxidation to NO_2 and the selective catalytic reduction (SCR) of NO_x in excess oxygen. Three different types of hydrocarbon reductants were studied, namely, propane, propylene and the long-chain hydrocarbon decane. For comparison, the performance of CuO and CuO + Ag supported on alumina for the SCR of NO_x by propane was also studied. This data was analyzed and discussed with reference to the information concerning the surface properties of these systems presented in Part 1 of this series. In general, for the same system, the maximum level of NO_x conversion and temperature of maximum NO_x conversion is strongly dependent upon the type of reducing agent. No universal relation was found between the surface density of coordinatively unsaturated cations able to activate hydrocarbons and the activity of the catalysts for the SCR reaction. In part, it can be explained by blocking the surface sites in reaction media either by strongly bound nitrate species or by coke. Addition of silver was found to be of significance only in the case of strong interaction between the metallic and oxidic components. Such a factor as the strength of oxygen and nitrate complexes bonding with the surface copper/copper–silver oxidic species depending upon the type of support and methods of samples synthesis appears to be the most important for performance of the systems studied in NO_x-selective reduction by hydrocarbons in the presence of excess oxygen.

Key Words: **NO_x selective reductions by propane; propylene; decane; supported copper oxide; promotion by silver; mesoporous stabilized zirconia supports.**

INTRODUCTION

Zirconia-supported transition metal cations are known to possess a reasonably good catalytic activity in the reactions of NO_x-selective reduction by hydrocarbons in the excess of oxygen (1–6). In earlier studies, transition metal cations were either incorporated into the bulk of zirconia via the coprecipitation route or supported on monoclinic/tetragonal modifications of ZrO_2 with a moderate (up to 60 m^2/g) surface area. In the reaction of NO_x-selective reduction by propylene, catalytic performance of those systems was found to be comparable to that of cation-exchanged ZSM-5 (1–3, 6). However, in the case of propane as reducing agent, those systems were only moderately active (1–3). For NO_x reduction by long-chain hydrocarbons such as decane, a good performance was obtained only in the case of copper supported on sulfated zirconia (4, 5). Hence, for different types of hydrocarbons as reducing agents, performance of zirconia-supported transition metal cations seems to be quite different. In part, it can be assigned to specificity of reaction mechanism depending upon the mode of hydrocarbon activation and subsequent transformation of intermediates on different types of isolated/clustered cations known to be present on the surface of those systems (1–7). Since coordination and clustering degree of supported transition metal cations are well known to depend upon the support chemical nature, bulk/surface structure and its disordering, specific surface area and pore structure, systematic studies of the effect of those parameters on transition metal cations catalytic properties in the NO_x selective reduction by different hydrocarbons is certainly of a great interest from the fundamental and applied point of view. In our previous communication (7), mesoporous zirconia samples stabilized by alkaline-earth cations with supported copper cations and silver were synthesized and characterized

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by using a combination of such sophisticated methods as XPD, TEM, EXAFS, SAXS, FTIRS of adsorbed CO, and TPD of NO_x. The aim of the present paper is to characterize the performance of these systems in the SCR of NO_x by hydrocarbons using three different types of reductant and to elucidate the features responsible for the catalytic properties of these systems.

METHODS

The methods of sample synthesis and their properties are described in the first paper of the series (7). The properties of the catalysts for the NO_x SCR and NO oxidation to NO_2 by O_2 reactions were tested in flow microreactors using procedures described previously (8–11) at GHSV 4000/h–12,000/h (0.1% C_3H_8 + 0.1% NO + 1% O_2 in He, feed 1), 18,000/h (0.2%C_3H_8 + 0.2% NO + 2.5% O_2 in N_2, feed 2), 18,000/h (0.2%C_3H_6 + 0.2% NO + 2.5% O_2 in N_2, feed 3), 11,200/h (0.05%$C_{10}H_{22}$ + 0.15% NO in air, feed 4), and 30,000/h (1%NO + 1% O_2 in He, feed 5). The error in determining NO conversion for feed 5 using FTIRS [10] was found to be ca. 2 rel%, whereas for feeds 1–4, where GC and a NO_x chemiluminescence analyzer were used (9, 11), corresponding error was found to be around 5 rel%.

RESULTS

1. No Oxidation into NO_2

Figure 1 shows typical results obtained for pure supports and supported Ag–CuO systems. For pure supports, the rates of NO oxidation are rather low, being only slightly dependent upon the type of substituting cation. Even at the highest temperatures used in our experiments, NO conversion into NO_2 is lower than the equilibrium value (10). At high temperatures, the rate of NO oxidation decreases in the order $BaO–ZrO_2 > SrO–ZrO_2 > CaO–ZrO_2$, which correlates with the degree of structural disordering of these systems determined primarily by the size of substituting cation (7). In addition, at the low content of alkaline-earth cations used here, in the surface layer, the energy of the Zr–O bond estimated by the ratio of the ion currents ZrO^+/Zr^+ was found to increase from Ba- to Ca-modified samples (8). Hence, at high temperatures, the rate of NO oxidation into NO_2 appears to be determined by rather strongly bound oxygen, which is also responsible for the relative stability of such possible intermediates in NO_x HC-SCR as nitrite–nitrate species (9, 10). At low temperatures, molecular oxygen species could be important for NO oxidation. At least, for $BaO–ZrO_2$ sample, the decrease of NO conversion with temperature can be explained by desorption of these weakly bound forms.

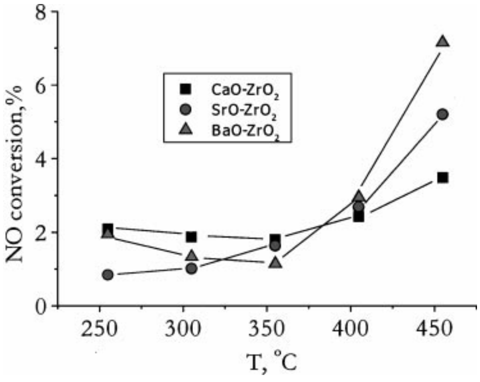

FIG. 1. Temperature dependence of NO oxidation into NO_2 on mesoporous zirconia supports stabilized by alkaline-earth cations; feed 5.

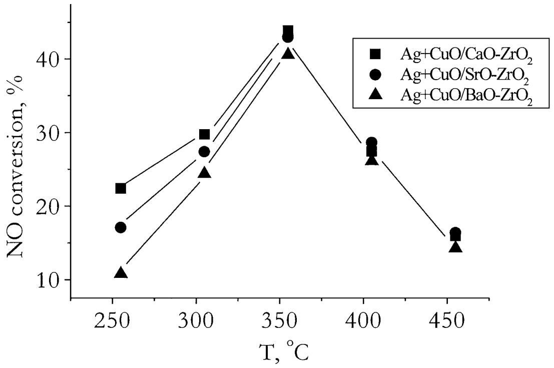

FIG. 2. Temperature dependence of NO oxidation into NO_2 on Ag + CuO/*Me*O–ZrO_2 samples; feed 5.

For Ag + CuO/MeO–ZrO_2 samples, the rates of NO oxidation are strongly increased as compared with supports (Fig. 2). At low temperatures, conversion decreases in the order Ag + CuO/CaO–ZrO_2 > Ag + CuO/SrO–ZrO_2 > Ag + CuO/BaO–ZrO_2. This order does not correlate with adsorption properties of these systems with respect to CO or NO (7). At high temperatures, NO conversion is determined by equilibrium being insensitive to the nature of samples. Hence, at temperatures exceeding 350°C, both the NO oxidation into NO_2 and the NO_2 decomposition reactions are very fast. This agrees with the TDP data, indicating that for these samples, $T_{\max}$ of nitrates decomposition are usually in the range of 350–380°C (7).

2. Selective NO_x Reduction by Propane

For pure supports, the results are presented in Fig. 3. In the first approximation, the rates of NO reduction and propane oxidation correlate with the surface disordering of these samples (7) and the rate of NO oxidation into NO_2 (vide supra). Hence, for modified zirconias, the rate of NO selective reduction can be determined by the bonding strength of nitrate species affecting their reactivity, as was suggested in (8, 9), and/or the rate of propane activation,

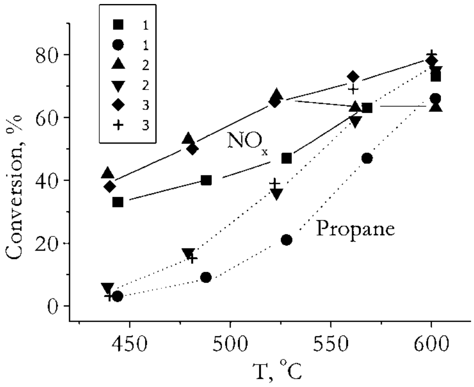

FIG. 3. Temperature dependence of NO conversion into N_2 and propane oxidation into CO_x on mesoporous *Me*O–ZrO_2 samples. *Me* = Ca (1), Ba (2), and Sr (3). Feed 1, GHSV 4000/h.

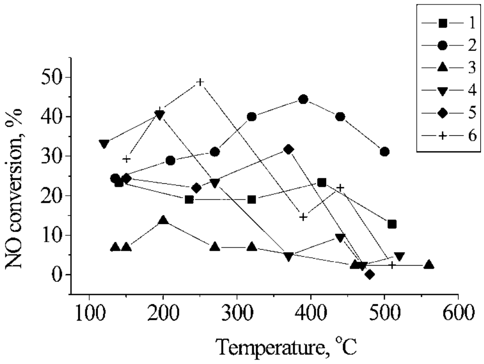

FIG. 5. Temperature dependence of NO selective reduction into N_2 by propane in the excess of oxygen (feed 2, GHSV 18,000/h) on *Me*O–ZrO_2 samples loaded with 0.2 wt% copper (ion exchange route, 1–3) or with 2 wt% Ag + 5wt% CuO (consecutive impregnation route, 4–6). *Me* = Ca (1, 4), Sr (2, 5), and Ba (3, 6).

both being determined by the bonding strength of oxygen in the surface layer.

For CuO/MeO–ZrO_2 systems prepared via the impregnation route, in the first approximation, the rates of NO-selective reduction by propane are comparable (Fig. 4), this is in agreement with the conclusions of Pietrogiacomi *et al.* (6) about the low sensitivity of the turn over rates of SCR reactions for copper-supported zirconia samples. Subtle differences, namely, a high rate of propane combustion for the CuO/CaO–ZrO_2 system leading to decreased NO_x reduction, especially at enhanced (>350°C) temperatures, can be explained by the highest surface density of coordinatively unsaturated Cu^+ centers (7), leading to a high rate of the radicals generation.

In the case of Ag + CuO/MeO–ZrO_2 systems prepared via the consecutive impregnation, a pronounced interaction between the metallic and oxidic components forming either mixed clusters or even microphases of interaction (7) helps to shift the maximum of NO conversion to lower (200–250°C) temperatures (Fig. 5). It seems to be mainly explained by the decrease of the oxygen bonding strength due to clustering and formation of mixed oxidic species (7), leading to more efficient activation/conversion of propane (Fig. 6). In addition, the bonding strength of bridging and/or bidentate nitrates is also decreased for these systems (7), thus helping to increase the low-temperature activity. Indeed, the Ag + CuO/BaO–ZrO_2 sample, which exhibits the highest level of low-temperature activity, is characterized by the lowest thermal stability of nitrate surface complexes (7). Moreover, for this sample, the lowest frequency of the carbonyl band was observed, implying pronounced interaction between the copper and silver oxidic species (7).

For Ag + CuO/MeO–ZrO_2 samples prepared via photodeposition, as compared with samples prepared via successive impregnation, the range of the efficient operation is shifted to higher (350–450°C) temperatures (Figs. 7 and 8). For the former samples, the content of copper and silver (in the range of 0.2% Ag + 3% CuO) is somewhat lower

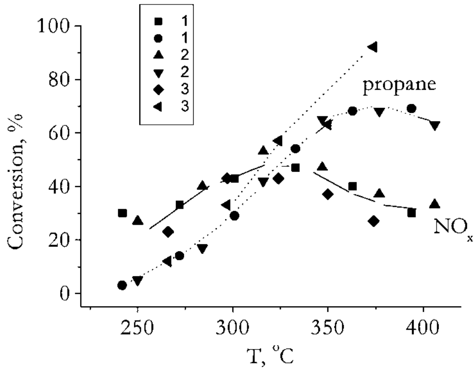

FIG. 4. Temperature dependence of NO conversion into N_2 and propane oxidation into CO_x on *Me*O–ZrO_2 samples loaded with 5 wt% of CuO (impregnation route). *Me* = Sr (1), Ba (2), and Ca (3). Feed 1, GHSV 4000/h.

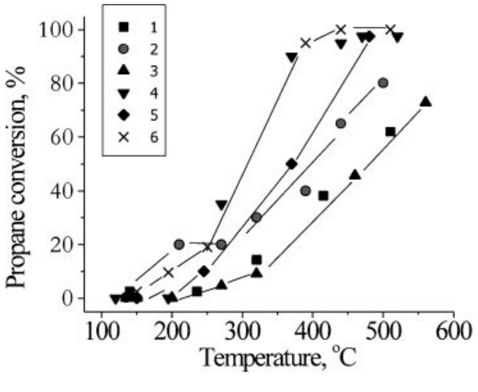

FIG. 6. Temperature dependence of propane conversion into CO_2 on *Me*O–ZrO_2 samples loaded with 0.2 wt% copper (1–3) or with 2 wt% Ag + 5 wt% CuO (4–6). Feed 2, GHSV 18,000/h. *Me* = Ca (1, 4), Sr (2, 5), and Ba (3, 6).

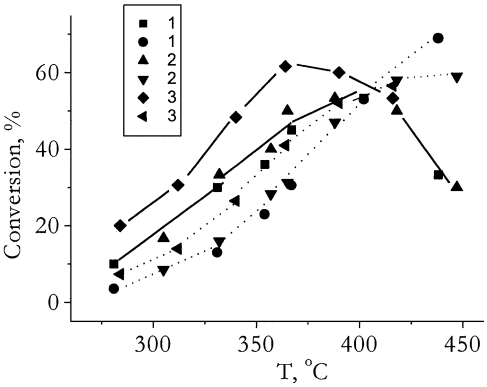

FIG. 7. Temperature dependence of NO conversion into N_2 (solid lines) and propane oxidation into CO_x (dashed lines) on *Me*O–ZrO_2 samples loaded with silver and copper via consecutive photoassisted deposition route. Sample composition: 0.8% Ag + 3 wt% CuO/BaO–ZrO_2 (1), 0.2% Ag + 3.1 wt% CuO/CaO–ZrO_2 (2) and 0.2 wt% Ag + 2.5 wt% CuO/SrO–ZrO_2 (3). Feed 1, GHSV 14,000/h.

as compared with that for the latter (2% Ag + 5% CuO). Hence, a lower degree of copper oxidic species clustering and a less pronounced effect on their properties of a smaller amount of loaded silver is expected for samples prepared via the photodeposition route. Though more detailed and systematic studies are certainly required to elucidate all fine structural features of systems prepared by using photodeposition, in the first approximation, a higher intensity of Cu^+–CO and Cu^{2+}–CO bands revealed for these systems and a higher frequency of Cu^+–CO band (7) certainly agrees with conclusion about higher dispersion and lower clustering degree of copper oxidic species for these samples. A lower rate of propane oxidation at relatively low (<350°C) temperatures for sample prepared via the photodeposition route (Fig. 8) implies a lower ability of less aggregated copper oxidic species to activate propane by its partial oxidation, which can be assigned to a higher bonding strength of oxygen in this case. According to our previous experience (7, 12), a higher bonding strength of oxygen with supported copper oxidic species is usually reflected in their lower reducibility by CO at low (77 K) temperatures and higher frequency of bands corresponding to complexes of CO with Cu^+ cations of those species. Indeed, for Ag + CuO/MeO–ZrO_2 samples prepared via photodeposition, at full CO coverage, those bands are situated at ~2115–2117 cm^{-1}, which is certainly higher than ~2100 cm^{-1} position for samples prepared via the consecutive impregnation (7). Rather close catalytic performance of catalysts prepared via the photodeposition route (Fig. 7) agrees well with comparable surface densities of coordinately unsaturated Cu^+ centers probed by this test molecule (7). Further, a somewhat higher performance of Sr-stabilized zirconia supported catalyst correlates with a higher intensity of corresponding carbonyl band (7). At present, for these systems, the effect of silver (if any) is not apparent, probably, due to independent location of copper and silver oxidic species on the surface (vide infra).

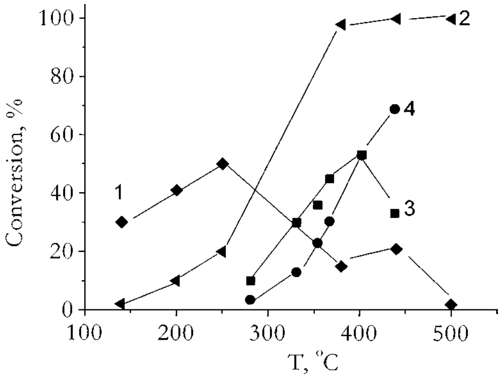

FIG. 8. Comparison of performance of Ag, CuO-containing samples prepared on BaO–ZrO_2 support via photoassisted deposition (1, 2) and impregnation (3, 4) routes. 1, 3-NO_x into N_2; 2, 4-propane into CO_2. Active components: 0.8% Ag + 3 wt% CuO (1, 2) and 2 wt% Ag + 5 wt% CuO (3, 4). 1, 2, Feed 1; 12,000/h; 3, 4, feed 2, 18,000/h.

In the case of alumina as a support (Fig. 9), for the same method of photoassisted deposition of active components,

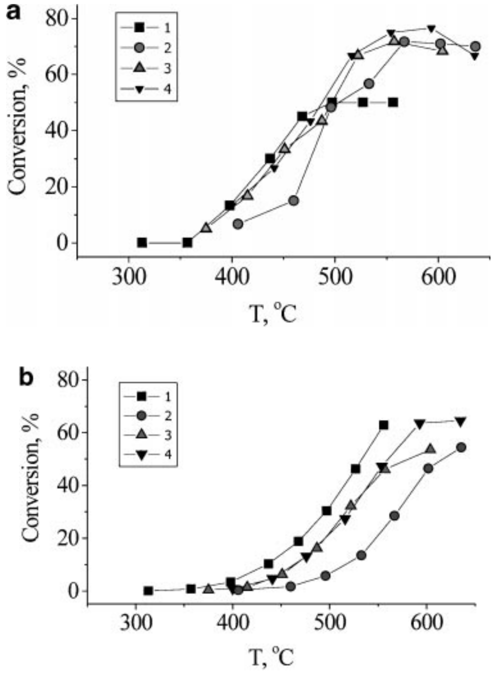

FIG. 9. (a) Temperature dependence of NO conversion into N_2 on alumina loaded with copper (1, 3) or silver + copper (2, 4) via consecutive photoassisted deposition route. Copper was supported from nitrate solution (1, 4) or from acetate solution (3, 4). Copper oxide content is equal to 0.7 wt% (1, 2) or to 0.5 wt% (3, 4). Silver content is equal to 0.6 wt% (2) or to 0.3 wt% (4). Feed 1, 12,000/h. (b) Temperature dependence of propane oxidation into CO_2 on alumina loaded with copper or silver + copper via the consecutive photoassisted deposition route. Curve designation is the same as in (a). Feed 1, 12,000/h.

operating temperatures are even higher than for zirconia-supported samples. Thus, at temperatures in the range of 350–400°C, where performance of zirconia-supported samples reaches a maximum, the activity of alumina-supported samples is still low. Note that at middle (∼400°C) temperatures, for samples without silver, the increase of the copper content from 0.5 to 0.7% (samples prepared using copper nitrate and acetate solutions, respectively) has a very little effect on the degree of NO conversion, while considerably enhancing propane oxidation. At temperatures exceeding 480°C, the degree of NO conversion is lower for samples with a higher copper content, probably, due to a higher rate of propane combustion. The results for higher (1 wt%) copper loading on alumina presented in (9) as well as results obtained within this work for 1.5% CuO/alumina sample, not shown here for brevity, demonstrate that, in every case, increasing the copper content does not help to increase the low-temperature performance and even deteriorates the high-temperature performance. Hence, for copper/alumina catalysts, a shift of the range of efficient performance in the HC–NO_x reactions to higher temperatures as compared with copper/zirconia systems could not be explained by a lower loading alone. Moreover, as was shown in (7), for samples with copper loading in the range of 0.5–2 wt%, the density of Cu^+ centers probed by the FTIRS of adsorbed CO molecules and related to the unit weight of copper is comparable for both supports. Hence, the reason for the different activity range of alumina- and zirconia-supported catalysts cannot be explained exclusively by a different degree of copper clustering dependent upon its surface concentration. From the mechanistic point of view, the most essential difference seems to be the bonding strength of nitrite–nitrate species, which were shown to be intermediates in the reaction of NO_x reduction by propane (9, 13, 16, 17). Indeed, for the copper/alumina system, the TPD maximum corresponding to nitrates decomposition is situated at ∼450°C (9), while for CuO/zirconia it is shifted to lower (360–380°C) temperatures (7). Hence, the temperature of nitrate complexes decomposition practically coincides with the ranges of the most efficient performance of these systems, which appears to be the general feature of reactions with participation of strongly bound intermediates (9). As was shown in (7, 12), among alumina-supported copper oxidic species, two-dimensional clusters dominate, which are nearly absent for the case of zirconia support. In these clusters, all oxygen atoms are strongly bound with two copper cations (12). As the result, bridging or bidentate nitrates located at these clusters have a higher bonding strength (9) and lower reactivity as compared with ad-NO_x species on CuO/zirconia catalysts, where isolated copper species and three-dimensional copper oxidic clusters appear to dominate (7).

The effect of silver addition was quite different for the two copper/alumina samples studied here. When loadings of both copper and silver are low, silver appears to be deposited on the free sites of support not affecting the properties of copper oxidic species (7). Since silver cations are known to strongly retain nitrate species, they are not able to activate propane up to 450°C (10, 14, 15), and, hence, participate in the SCR of NO_x. As a result, NO_x and propane conversion were not changed appreciably after silver addition (Fig. 9).

For a sample with a higher content of copper (0.7%), a degree of copper clustering is somewhat higher, which follows from a lower intensity of Cu^+–CO carbonyl band (7). In this case, silver is mainly deposited on copper clusters blocking coordinatively unsaturated copper cations (7). As the result, the rate of propane consumption was strongly hindered (Fig. 9), which decreased NO conversion at temperatures <450°C as well. However, at higher temperatures, the effect of silver addition on NO conversion was certainly beneficial in this case, probably due to conjugation between functions played by metallic and oxidic components leading to a more efficient generation of such intermediates as organic nitrocompounds [10].

3. Selective NO_x Reduction by Propylene

The data presented in Figs. 10 and 11 imply that for the systems considered here, in the first approximation, the catalytic properties in the reactions of NO_x reduction by propane and propylene are similar. Thus, the highest low-temperature activity in both reactions is observed for Ag + CuO/BaO–ZrO_2 system (vide supra). However, some difference is observed for samples with a low copper content without silver: for the case of propylene as reductant, due to its easier activation as compared with propane, silver is not required to achieve a high level of activity at low/middle temperatures. As was shown in our previous work by using *in situ* IR studies (11), two routes of NO_x

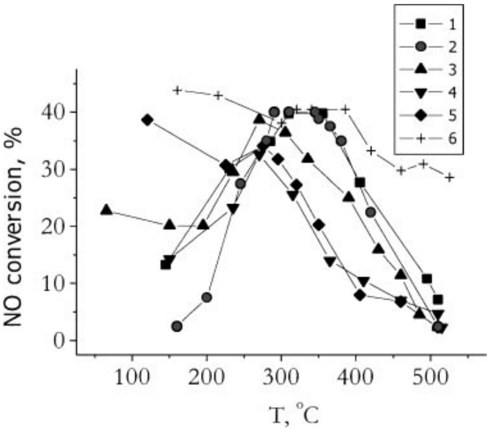

FIG. 10. Temperature dependence of NO selective reduction into N_2 by propylene in the excess of oxygen (feed 3) on *Me*O–ZrO_2 samples loaded with 0.2 wt% CuO (ion exchange route, 1–3) or with 2 wt% Ag + 5 wt% CuO (consecutive impregnation route, 4–6). *Me* = Ca (1, 4), Sr (2, 5), or Ba (3, 6). Feed 3, 18,000/h.

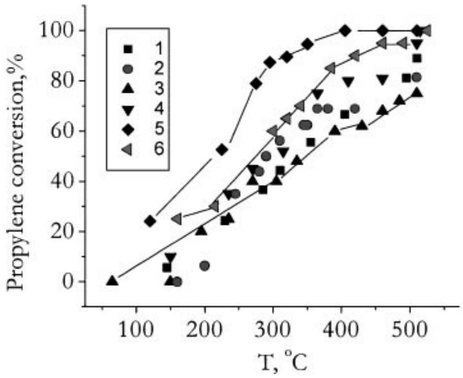

FIG. 11. Temperature dependence of propylene conversion into CO_2 on *Me*O–ZrO_2 samples loaded with 0.2 wt% CuO (1–3) or with 2 wt% Ag + 5 wt% CuO (4–6). Feed 3, 18,000/h. *Me* = Ca (1, 4), Sr (2, 5), or Ba (3, 6). Feed 3, 18,000/h.

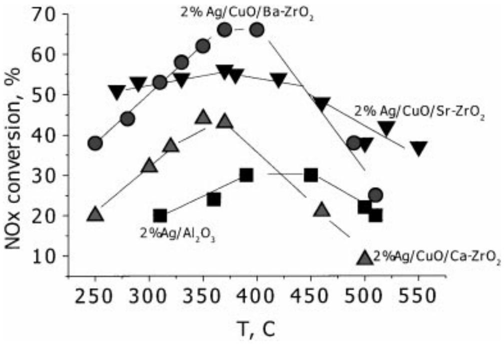

FIG. 13. Temperature dependence of NO selective reduction into N_2 by decane in the excess of oxygen on *Me*O–ZrO_2 samples loaded with 2% Ag + 5 wt% CuO (impregnation route) as compared with 2 wt% Ag/alumina sample. Feed 4, 11,200/h.

reduction by propylene are realized in the case of supported copper systems: a first one includes interaction of propylene with adsorbed nitrite-nitrate species (similar to that occurring in the case of propane as reductant (13, 16, 17), while the second one proceeds by NO interaction with a coke deposited on the support. Hence, the second route, which is expected to be the most essential in the case of low copper loadings, is less sensitive to the state of supported copper oxidic species.

4. Selective NO_x Reduction by Decane

For this reaction, the catalytic behavior of systems considered here is more complicated. There is certainly a trend in increasing the activity with the increase in the copper content (Fig. 12); nevertheless, the reason for the absence of activity for systems having a good performance in the NO_x reduction by propane is not so clear at present. The absence of activity for a 5% CuO/BaO–ZrO_2 sample appears to correlate with a low density of coordinatively unsaturated Cu^+ centers due to aggregation of copper cations into bulky copper oxidic species (7). In this case, the rate of decane activation on those sites is expected to be too low to ensure a reasonable activity. Surface coking/carbonization of the surface of zirconia-supported samples depending upon the density of relatively strong Lewis/Brønsted acid sites is worth considering as a possible reason for deactivation as well.

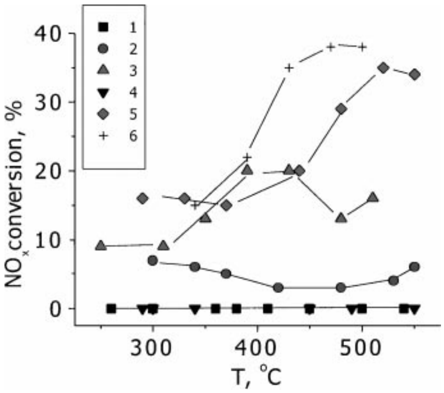

FIG. 12. Temperature dependence of NO-selective reduction into N_2 by decane in the excess of oxygen on *Me*O–ZrO_2 samples loaded with 0.2 wt% CuO (ion exchange route, 1–3) or with 5 wt% CuO (impregnation route, 4–6). *Me* = Sr (1, 5), Ca (2, 6), or Ba (3, 4). Feed 4, 11,200/h.

Silver addition to copper via impregnation greatly improves performance of catalysts on all supports (cf. Figs. 12 and 13). Comparison with performance of a specially prepared Ag/alumina catalyst (Fig. 13) demonstrates that this enhancement of activity is of a nonadditive nature. The increase of performance due to modification by silver correlates with the increase in the density of coordinatively unsaturated Cu^+ sites (7), which agrees with suggestion about the role of these centers in the decane activation (vide supra). Indeed, the order of activity observed here (Ag + CuO/BaO–ZrO_2 > Ag + CuO/SrO–ZrO > Ag + CuO/CaO–Zr) is the same as for the case of propane as reducing agent (vide supra), which appears to be activated primarily on coordinatively unsaturated Cu^+ sites (17). Another important factor worth considering is the decrease of the bonding strength and increase of the bidentate and bridging nitrates reactivity due to silver addition (7), which certainly help to ensure a high performance of modified systems in the reaction of NO_x reduction by decane. At last, decrease of the oxygen bonding strength in silver-modified samples (7) could help to avoid the surface coking suggested above as one of the reason for the absence of activity for some nonpromoted samples.

DISCUSSION

1. The Role of Support

The role of support appears to be mainly determined by its ability to affect the type and size of various oxidic species due to the known effect of interaction between the oxide species and supports (11). At the same level of copper loading and the same preparation procedure, partially stabilized zirconias as supports favor domination of such species as isolated copper cations and small reactive three-dimensional clusters, while for alumina, two-dimensional copper oxidic clusters are the most abundant (7, 11). As a result, for copper oxidic species, on average, the bonding strength of oxygen and reactive nitrite–nitrate intermediates is higher for the case of alumina-supported systems, which is reflected in higher operating temperatures in the NO_x selective reduction by hydrocarbons in the excess of oxygen.

For zirconia partially stabilized by the alkaline-earth cations studied here, the nature of the guest cation only moderately affects the structural features of supported copper oxidic species, especially in the case of higher copper loadings. As a result, in the first approximation, in the reactions of selective NO reduction by propane and propylene, catalytic properties of copper on these supports are comparable. However, stronger effects are observed in the case of decane as reducing agent, which certainly deserve further studies.

At the same operational parameters (space velocities and feed composition), the maximum degree of NO_x reduction is comparable for alumina- and zirconia-supported copper catalysts. However, from the practical application point of view, lower operating temperatures for zirconia-supported samples appear to be more attractive.

2. *The Role of Interaction between the Metallic and Oxidic Components*

Analysis of the data obtained here allows preliminary conclusions concerning the role of oxidic (copper) and metallic (silver) components in the reactions of NO_x reduction by hydrocarbons to be drawn.

When the interaction between silver and copper oxidic clusters is negligible, silver addition does not effect the catalyst performance in the NO_x reduction. This is explained as follows:

(i) For catalysts containing copper cations, the rate of NO oxidation into NO_2 then converted to reactive nitrite–nitrate species is high (vide supra), so silver addition does not affect it. As a result, contrary to the case of silver/alumina system (10), the surface coverage by reactive intermediates including nitrite–nitrate species and organo-NO_x compounds is expected not to change noticeably.

(ii) The rate of hydrocarbon activation/oxidation is also not expected to be increased in the case of a weak (if any) interaction between silver and copper oxidic species. Indeed, the highest rates of hydrocarbon oxidation are typical for three-dimensional copper oxidic clusters fixed on support due to decreased bonding strength of oxygen (18). As follows from our data for zirconia-supported copper oxide (vide supra), when such species dominate, appreciable propane conversions are achieved at temperatures in the range of 300–350°C. At low (up to 2 wt%) loading of silver on alumina, silver exists as oxidic clusters stabilized by support (19). These species have a moderate ability to activate hydrocarbons. Thus, for ∼2 wt% Ag/alumina catalyst, at GHSV ∼ 13,000/h–18,000/h, even in mixtures with a great excess of oxygen (∼10%), detectable (∼10%) propane conversions were achieved only at temperatures ∼400–450°C (14, 15). Hence, for catalysts with silver and copper oxidic species independently distributed on the support, nonadditive effects in the hydrocarbons activation are not expected as well.

(iii) The strength of the reactive nitrite–nitrate species bonding with silver cations is comparable or even higher (14) than with copper or alumina cations (9, 10). Hence, at temperatures of supported copper catalysts efficient performance, the independent route of NO_x reduction via propane interaction with ad-NO_x species strongly bound with silver cations is not expected to appreciably increase the degree of NO_x conversion.

When silver clusters are juxtaposed on copper oxidic species, as is revealed in this work for the case of alumina-supported catalysts, catalytic properties are changed in a complex fashion: the rate of propane oxidation is decreased in all the temperature range studied, the low-temperature NO_x conversion is decreased as well, while the high-temperature conversion is improved. These features are explained by the preferential location of silver species on coordinatively unsaturated copper cations thus blocking them and retarding in such a way propane activation. At high temperatures, when propane can be selectively activated on silver, the level of NO_x conversion is enhanced due to suppression of a deep oxidation route.

When interaction between silver and oxidic copper clusters is pronounced, which is achieved by using a special preparation procedure, it helps to enhance performance, especially in the low- and middle-temperature ranges, mainly due to the following reasons:

(i) Due to decrease of the bonding strength of oxygen located on mixed oxidic clusters, the rate of hydrocarbon activation is increased.

(ii) In mixed clusters, the bonding energy of nitrite–nitrate species is changed in a nonadditive manner, so that population of forms with the intermediate bonding strength is usually increased, while that of a high bonding strength-decreased.

3. *The Role of the Type of Reducing Agent*

For the systems considered here, in the first approximation, for different reducing agents, the orders of activity were rather similar. The most important feature of samples studied here is that they ensure a high (up to 70%) level of NO conversion into N_2 at rather low (350–370°C) temperatures in the excess of oxygen using propane as reductant. This low-temperature level of performance approaches that for the overexchanged sample of Cu-ZSM-5 ($\sim$2 wt% of Cu, $Si/Al_2 \sim 50$) (20) tested earlier with the same reductant and the same feed composition ($\sim$100% NO conversion into N_2 at 300–330°C). Though the highest level of activity was obtained here for silver-promoted samples, a good NO_x conversion (up to 50%) was also observed for samples without silver. Earlier (1–3, 6), mixed copper–zirconia oxide samples were demonstrated to be rather active in the reaction of NO-selective reduction by propylene (NO conversion up to 70% at GHSV $\sim$10,000/h), while being only moderately active with propane as reductant (conversion not exceeding 10% at 450°C). This difference clearly implies that any comparison between the performance of catalysts in NO_x-selective reduction by different hydrocarbon should take into account not only their chemical composition but the microstructure as well. In our case, partially stabilized mesoporous cubic zirconia samples are used as a support, and distribution of copper cations between species with a different copper coordination and clustering degree certainly differs with that for previously studied coprecipitated copper–zirconia samples (1–3). Besides, it is affected by the nature of stabilizing alkaline-earth cations as well (7). Similar effects appear to take place in the case of copper supported on the sulfated zirconia surface. In this case, the maximum level of NO_x-selective reduction by propane was increased up to 40%, though being shifted to higher ($\sim$500–550°C) temperatures (21).

In the case of NO-selective reduction by propane on copper-containing catalysts, breaking of the C–H bond is considered to be the rate-determining stage followed by interaction of the activated fragment with nitrite–nitrate species yielding an organic nitrocopound (13, 16, 17). This stage can be facilitated either by increasing the coordination unsaturation of the copper cations or by increasing the surface oxygen reactivity via decreasing its bonding strength. In addition, the bonding strength of reactive intermediates—nitrate–nitrate species—is known to decrease with decreasing surface oxygen bonding strength, while corresponding reactivity of these species increases (9). Another important factor is that coordinatively unsaturated sites can be blocked in the reaction media by strongly bound nitrate species, thus hindering hydrocarbon activation. The last factor appears to be decisive for the low-temperature performance of samples studied here in the reaction of NO_x-selective reduction by propane: the highest level of NO_x conversion was obtained for 0.2% $CuO/SrO–ZrO_2$ and 2% Ag + 5% $CuO/BaO–ZrO_2$ sample with the lowest surface coverage by nitrate species (7). For catalysts with a low copper content prepared via the cation exchange, for which isolated copper cations dominate, thermally stable bridging nitrates can be bound simultaneously with copper and zirconium cations as well as with the guest cations such as Ba located at the surface (7). Certainly, the decrease of the copper–oxygen bonding strength due to silver incorporation into copper oxidic clusters also helps to decrease the thermal stability of nitrates (vide supra), and, hence, their steady-state coverage at a given temperature, thus enhancing the rate of hydrocarbons activation.

In the case of more reactive propylene as reductant, its activation is known to be less demanding; hence, copper cation clustering degree or the surface site blocking by strongly bound nitrates appear to be less important for the low-temperature performance. As the result, samples with a low copper loading prepared via cation exchange have identical maximum values of NO_x conversion, which are even somewhat higher than those for some silver-promoted samples with a higher copper loading. In this respect, our results agree with conclusions of Pietrogiacomi *et al.* (7) about the highest turnover rates in the NO_x selective reduction by propylene for isolated copper cations dispersed on monoclinic zirconia support. However, we must also keep in mind that for the route of NO_x reduction by propylene proceeding via No interaction with the coke deposited on support (11, 22, 23), any relation between the catalyst performance and characteristics of a “clean” surface hardly could be straightforward. At low temperatures, coke can block the surface, thus decreasing performance of catalysts with a low oxidizing ability. Indeed, silver addition to $CuO/BaO–ZrO_2$ system was found to make it the most active catalyst in the reaction of NO_x reduction by propylene in a very broad (150–500°C) temperature range. It implies that decreasing the oxygen bonding strength with copper–silver oxidic clusters is favorable for a good catalysts performance in this reaction as well.

For the reaction of NO_x reduction by decane, the low-temperature performance of copper/zirconia samples not promoted by silver is as good as that seen with Cu/mordenite (24). The absence of activity for some samples reasonably active with propane and propylene as reductants suggests the surface blocking by coke and/or carbonates. Indeed, strong deactivation of BEA zeolitic catalysts in the decane NO_x SCR due to coking was earlier observed by Delahay *et al.* (25). Among inactive samples, those with a low density of coordinatively unsaturated Cu^+ centers are present, thus suggesting their importance for the decane activation as well. However, performance is greatly improved by the silver addition, which helps thus to approach the maximum level of NO_x reduction by decane at moderate (300–350°C) temperatures similar to that for copper/sulfated zirconia (4, 5), Cu/mordenite (24), or copper-exchanged beta zeolite (25). In the case of decane as reducing agent, sample modification by silver via a special impregnation procedure helps to increase the surface density of Cu^+ centers due to bulky oxidic cluster redispersion and/or formation of mixed copper–silver oxidic microphases. Silver addition appears also to be important for decreasing the surface blocking by coke via facilitation of its oxidation by weakly bound oxygen (25). Certainly, further studies are required to prove such a suggestion.

Since the highest level of low-temperature activity in all three reactions was achieved by the same Ag + CuO/BaO–ZrO_2 sample with the highest degree of interaction between copper and silver oxidic species (7), such an interaction appears to be important for ensuring a good performance in NO_x selective reduction by different hydrocarbons.

CONCLUSIONS

In the reaction of NO_x selective reduction by hydrocarbons (propane, propylene, and decane), catalytic performance of zirconia-suported copper oxidic species including those promoted by silver appears to be mainly determined by their local structure and composition affecting the bonding strength of oxygen and strongly bound nitrate species. In general, for the same system, the maximum level of NO_x conversion and temperature of maximum NO_x conversion is strongly dependent upon the type of reducing agent. No universal relation was found between the surface density of coordinatively unsaturated cations able to activate hydrocarbons and the activity of catalysts for the HC-SCR. It can be explained by blocking the surface sites in reaction media either by strongly bound nitrate species or by coke. Addition of silver was found to be of significance only in the case of strong interaction between the metallic and oxidic components. Such an interaction helps to decrease the bonding strength of oxygen with mixed copper–silver oxidic species, thus decreasing the bonding strength of adsorbed nitrate species. When it takes place, in all three reactions studied here, the level of activity at moderate (250–350°C) temperatures approaches that for the most efficient copper-containing systems tested up to date such as Cu-ZSM-5, Cu/sulfated zirconia Cu/mordenite, or Cu-beta zeolite.

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REFERENCES

1. Bethke, K. A., Alt, D., and Kung, M. C., *Catal. Lett.* **25**, 37 (1994).
2. Bethke, K. A., Kung, M. C., Yang, B., Shah, M., Alt, D., Li, C., and Kung, H. H., *Catal. Today* **26**, 169 (1995).
3. Bethke, K. A., Li, C., Kung, M. C., Yang, B., and Kung, H. H., *Catal. Lett.* **31**, 287 (1995).
4. Figueras, F., Coq, B., Ensuque, E., Tachon, D., and Delahay G., *Catal. Today* **42**, 117 (1998).
5. Delahay, G., Ensuque, E., Coq, B., and Figueras, F., *J. Catal.* **175**, 7 (1998).
6. Pietrogiacomi, D., Sannino, D., Tuti, S., Ciambelli, P., Indovina, V., Occhiuzzi, M., and Pepe, F., *Appl. Catal. B* **21**, 141 (1999).
7. Sadykov, V. A., *et al.*, part 1.
8. Sadykov, V. A., Ivanova, A. S., Ivanov, V. P., Alikina, G. M., Kharlanov, A. N, Lunina, E. V., Lunin, V. V., Matyshak, V. A., Zubareva, N. A., and Rozovskii, A. Ya., *in* "Advanced Catalytic Materials" (P. W. Lednor, D. A. Nagaki, and L. T. Thompson, Eds.), Vol. 454, p. 199. Pittsburgh, PA, 1997.
9. Sadykov, V. A., Baron, S. L., Matyshak, V. A., Alikina, G. M., Bunina, R. V., Rozovskii, A. Ya., Lunin, V. V., Lunina, E. V., Kharlanov, A. N., Ivanova, A. S., and Veniaminov, S. A., *Catal. Lett.* **37**, 157 (1996).
10. Meunier, F. C., Breen, J. P., Zuzaniuk, V., Olsson, M., and Ross, J. R. H., *J. Catal.* **187**, 493 (1999).
11. Matyshak, V. A., Ukharskii, A. A., Il'ichev, A. N., Sadykov, V. A., and Korchak, V. N., *Kinet. Katal.* **40**, 116 (1999).
12. Tikhov, S. F., Sadykov, V. A., Kryukova, G. N., Paukshtis, E. A., Popovskii, V. V., Starostina, T. G., Anufrienko, V. F., Razdobarov, V. A., Bulgakov, N. N., and Kalinkin, A. V., *J. Catal.* **134**, 506 (1992).
13. Sadykov, V. A., Paukshtis, E. A., Beloshapkin, S. A., Alikina, G. M., Veniaminov, S. A., Netyaga, E. V., Bunina, R. V., Lunina, E. V., Lunin, V. V., Matyshak, V. A., and Rozovskii, A. Ya., *React. Kinet. Catal. Lett.* **65**, 113 (1998).
14. Yamaguchi, M., Goto, I., Wang, Zh. M, and Kumagai, M., *in* "Science and Technology in Catalysis," p. 372. Kodansha, Tokyo, 1999.
15. Satokawa, Sh., Yamaseki, K., Hoshi, F., and Yahagi, M., Yokota, H., Uchida, H., Furuyama, M., Sumiya, S., and Yoshida, K., *in* "Science and Technology in Catalysis," p. 375. Kodansha, Tokyo, 1999.
16. Matyshak, V. A., Baron, S. L., Ukharskii, A. A., Il'ichev, A. N., Sadykov, V. A., and Korchak, V. N., *Kinet. Catal.* **37**, 585 (1996).
17. Sadykov, V. A., Beloshapkin, S. A., Paukshtis, E. A., Alikina, G. M., Kochubei, D. I., Degtyarev, S. P., Bulgakov, N. N., Veniaminov, S. A., Netyaga, E. V., Bunina, R. V., Kharlanov, A. N., Lunina, E. V., Lunin, V. V., Matyshak, V. A., Rozovskii, A. Ya., and Pol. J., *Environ. Studies* **1**, 21 (1997).
18. Kung, M. C., and Kung, H. H., *Catal. Today* **30**, 5 (1996).
19. Bethke, K. A., and Kung, H. H., *J. Catal.* **172**, 93 (1997).
20. Metelkina, O. V., Lunin, V. V., Sadykov, V. A., Beloshapkin, S. A., Alikina, G. M., Lunina, E. V., and Kharlanov, A. N., *Neftekhimia* **40**, 108 (2000).
21. Pasel, J., Speer, V., Albrecht, Ch., Richter, F., and Papp, H., *Appl. Catal. B* **25**, 105 (2000).
22. Centi, G., Galli, A., and Perathoner, S., *J. Chem. Soc. Faraday Trans.* **92**, 5129 (1996).
23. Vergne, S., Berreghis, A., Tantet, J., Canaff, C., Magnoux, P., Guisner, M., Davias, N., and Noirot, R., *Appl. Catal. B* **18**, 37 (1998).
24. Coq, B., Tachon, D., and Figueras, F., *Catal. Lett.* **35**, 183 (1995).
25. Delahay, G., Coq, B., and Broussous, L., *Appl. Catal. B* **12**, 49 (1997).